



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

<p>(51) International Patent Classification ⁵ :</p> <p>C07C 281/14, 281/06, 251/76, 243/22, C07D 209/08, A01N 47/34, C07D 209/42, 215/58</p>	A1	<p>(11) International Publication Number: WO 92/06076</p> <p>(43) International Publication Date: 16 April 1992 (16:04.92)</p>																													
<table style="width: 100%; border: none;"> <tr> <td style="width: 50%; vertical-align: top; padding: 5px;"> <p>(21) International Application Number: PCT/US91/07091</p> <p>(22) International Filing Date: 2 October 1991 (02.10.91)</p> <p>(30) Priority data:</p> <table style="width: 100%; border: none;"> <tr> <td style="width: 30%;">593,172</td> <td style="width: 30%;">5 October 1990 (05.10.90)</td> <td style="width: 40%;">US</td> </tr> <tr> <td>594,928</td> <td>10 October 1990 (10.10.90)</td> <td>US</td> </tr> <tr> <td>631,585</td> <td>21 December 1990 (21.12.90)</td> <td>US</td> </tr> </table> <p>(60) Parent Applications or Grants</p> <p>(63) Related by Continuation</p> <table style="width: 100%; border: none;"> <tr> <td style="width: 30%;">US</td> <td style="width: 30%;">593,172 (CIP)</td> <td style="width: 40%;"></td> </tr> <tr> <td>Filed on</td> <td>5 October 1990 (05.10.90)</td> <td></td> </tr> <tr> <td>US</td> <td>594,928 (CIP)</td> <td></td> </tr> <tr> <td>Filed on</td> <td>10 October 1990 (10.10.90)</td> <td></td> </tr> <tr> <td>US</td> <td>631,585 (CIP)</td> <td></td> </tr> <tr> <td>Filed on</td> <td>21 December 1990 (21.12.90)</td> <td></td> </tr> </table> <p>(71) Applicant (for all designated States except US): E.I. DU PONT DE NEMOURS AND COMPANY [US/US]; 1007 Market Street, Wilmington, DE 19898 (US).</p> </td> <td style="width: 50%; vertical-align: top; padding: 5px;"> <p>(72) Inventors; and (75) Inventors/Applicants (for US only) : HARRISON, Charles, Richard [US/US]; 137 Aspen Drive, Newark, DE 19702 (US). LAHM, George, Philip [US/US]; 148 Fairhill Drive, Wilmington, DE 19808 (US). STEVENSON, Thomas, Martin [US/US]; 103 Iroquois Court, Newark, DE 19702 (US).</p> <p>(74) Agents: COSTELLO, James, A. et al.; E.I. du Pont de Nemours and Company, Legal/Patent Records Center, 1007 Market Street, Wilmington, DE 19898 (US).</p> <p>(81) Designated States: AT (European patent), AU, BE (European patent), CA, CH (European patent), DE (European patent), DK (European patent), ES (European patent), FR (European patent), GB (European patent), GR (European patent), IT (European patent), JP, LU (European patent), NL (European patent), SE (European patent), US .</p> <p>Published <i>With international search report.</i> <i>Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i></p> </td> </tr> </table>			<p>(21) International Application Number: PCT/US91/07091</p> <p>(22) International Filing Date: 2 October 1991 (02.10.91)</p> <p>(30) Priority data:</p> <table style="width: 100%; border: none;"> <tr> <td style="width: 30%;">593,172</td> <td style="width: 30%;">5 October 1990 (05.10.90)</td> <td style="width: 40%;">US</td> </tr> <tr> <td>594,928</td> <td>10 October 1990 (10.10.90)</td> <td>US</td> </tr> <tr> <td>631,585</td> <td>21 December 1990 (21.12.90)</td> <td>US</td> </tr> </table> <p>(60) Parent Applications or Grants</p> <p>(63) Related by Continuation</p> <table style="width: 100%; border: none;"> <tr> <td style="width: 30%;">US</td> <td style="width: 30%;">593,172 (CIP)</td> <td style="width: 40%;"></td> </tr> <tr> <td>Filed on</td> <td>5 October 1990 (05.10.90)</td> <td></td> </tr> <tr> <td>US</td> <td>594,928 (CIP)</td> <td></td> </tr> <tr> <td>Filed on</td> <td>10 October 1990 (10.10.90)</td> <td></td> </tr> <tr> <td>US</td> <td>631,585 (CIP)</td> <td></td> </tr> <tr> <td>Filed on</td> <td>21 December 1990 (21.12.90)</td> <td></td> </tr> </table> <p>(71) Applicant (for all designated States except US): E.I. DU PONT DE NEMOURS AND COMPANY [US/US]; 1007 Market Street, Wilmington, DE 19898 (US).</p>	593,172	5 October 1990 (05.10.90)	US	594,928	10 October 1990 (10.10.90)	US	631,585	21 December 1990 (21.12.90)	US	US	593,172 (CIP)		Filed on	5 October 1990 (05.10.90)		US	594,928 (CIP)		Filed on	10 October 1990 (10.10.90)		US	631,585 (CIP)		Filed on	21 December 1990 (21.12.90)		<p>(72) Inventors; and (75) Inventors/Applicants (for US only) : HARRISON, Charles, Richard [US/US]; 137 Aspen Drive, Newark, DE 19702 (US). LAHM, George, Philip [US/US]; 148 Fairhill Drive, Wilmington, DE 19808 (US). STEVENSON, Thomas, Martin [US/US]; 103 Iroquois Court, Newark, DE 19702 (US).</p> <p>(74) Agents: COSTELLO, James, A. et al.; E.I. du Pont de Nemours and Company, Legal/Patent Records Center, 1007 Market Street, Wilmington, DE 19898 (US).</p> <p>(81) Designated States: AT (European patent), AU, BE (European patent), CA, CH (European patent), DE (European patent), DK (European patent), ES (European patent), FR (European patent), GB (European patent), GR (European patent), IT (European patent), JP, LU (European patent), NL (European patent), SE (European patent), US .</p> <p>Published <i>With international search report.</i> <i>Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i></p>
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<p>(54) Title: SEMICARBAZONE ARTHROPODICIDES</p> <div style="text-align: center; margin: 20px 0;"> </div> <p style="text-align: right; margin-right: 50px;">(I)</p>																															
<p>(57) Abstract</p> <p>Arthropodically active compounds of formula (I) including all geometric and stereoisomers and agriculturally suitable salts thereof, wherein J, X, R¹, R⁶, Z and n are defined in the text; compositions containing them and use of said compounds to control arthropods.</p>																															

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⁺ Any designation of "SU" has effect in the Russian Federation. It is not yet known whether any such designation has effect in other States of the former Soviet Union.

5

TITLE

SEMICARBAZONE ARTHROPODICIDES

BACKGROUND OF THE INVENTIONField of the Invention

10 This invention concerns arthropodicial
semicarbazones and their use to control arthropods.

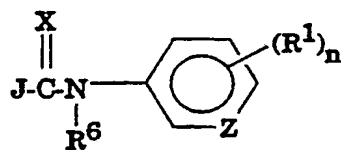
State of the Art

U.S. 3,885,042 discloses insecticidal benzylidene
semicarbazides. U.S. 3,712,914 and U.S. 3,753,680
15 disclose arylidene semicarbazides as herbicides. U.S.
3,274,115 discloses semicarbazides as germicides while
U.S. 3,558,654 discloses semicarbazone and
thiosemicarbazone quaternary salts as neuromuscular
blocking agents. DE 3,624,349 discloses substituted
20 arylhydrazones as pesticides. Japan Kokai 83/189,192
discloses organic phosphoric acid esters as insecticides.
WO 90/07495 discloses substituted semicarbazone
arthropodicides. U.S. 4,547,524 discloses benzoyl
hydrazone derivatives as insecticides. EP 3,913
25 discloses substituted benzophenone hydrazones as
insecticides. EP 254,461 discloses N-substituted
hydrazones as insecticides. U.S. 3,753,680 discloses
arylidene semicarbazones as herbicides. FR 1,455,835
discloses herbicidal hydrazine compositions. EP 34,010
30 discloses substituted thiosemicarbazones as plant growth
regulators. Japan Kokai 87/45,570 discloses aryl and
heterocyclic semicarbazones as herbicides.

SUMMARY OF THE INVENTION

The invention pertains to compounds of Formula I,
35 including all geometric and stereoisomers, agriculturally
suitable salts thereof, agricultural compositions
containing them and their use as arthropodicides in both

5 agronomic and nonagronomic environments. The compounds are:

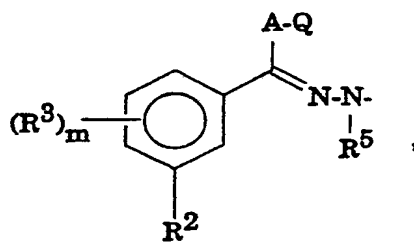


I

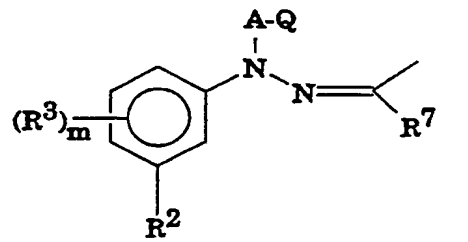
wherein

J is selected from the group

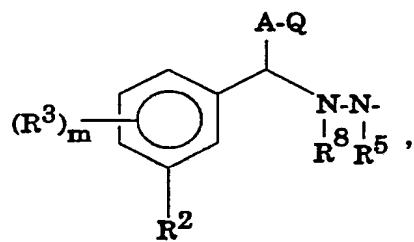
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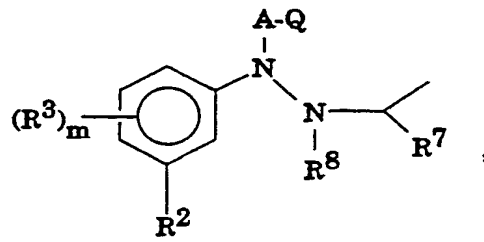
J-1



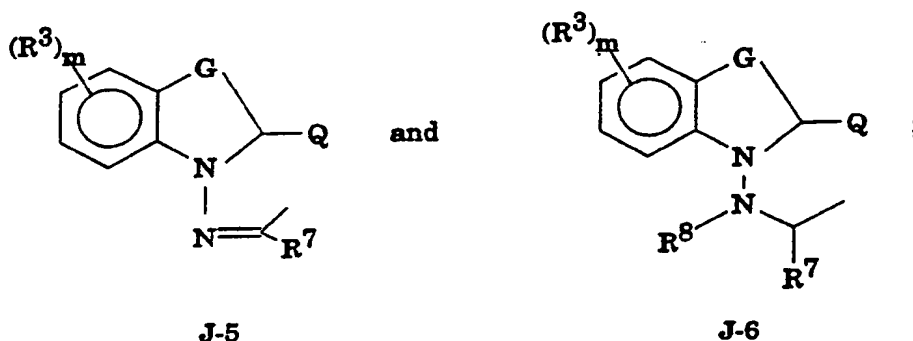
J-2



J-3



J-4



5

- A is a single bond or selected from the group
C₁-C₃ alkylene and C₃-C₆ cycloalkylene each of
which is optionally substituted with 1 or 2 R⁹;
- 10 G is C₁-C₂ alkylene optionally substituted with 1
or 2 CH₃;
- Q is selected from the group H, R⁹, phenyl
optionally substituted with (R⁴)_p, thienyl
optionally substituted with W, pyridinyl
optionally substituted with W, C₁-C₆ alkyl
optionally substituted with R⁹ and C₃-C₆
15 cycloalkyl optionally substituted with R⁹;
provided that when J is J-1 and A is methylene,
then Q is other than H;
- 20 X is selected from the group O and S;
Z is selected from the group N and CH;
- R¹, R², R³ and R⁴ are independently selected from
the group halogen, CN, SCN, R¹⁰, OR¹⁰, S(O)_qR¹⁰,
OSO₂R¹⁰, C(O)R¹⁰, CO₂R¹⁰, C(O)N(R¹⁰)R¹¹,
25 SO₂N(R¹⁰)R¹¹ and N(R¹⁰)R¹¹; and when m, n or p is
2, (R¹)₂, (R³)₂, (R⁴)₂ or R² and R³ when
attached to adjacent atoms can be taken together
as OCH₂O, OCF₂O, OCH₂CH₂O, OCH₂C(CH₃)₂O or
OCF₂CF₂O to form a cyclic bridge; provided that
30 when R² is Cl then R³ is other than Cl;

- 5 R^5 and R^6 are independently selected from the group
H, C_1 - C_6 alkyl, C_2 - C_6 alkoxyalkyl, CHO, C_2 - C_6
alkylcarbonyl, C_2 - C_6 alkoxycarbonyl, C_2 - C_6
haloalkylcarbonyl, C_1 - C_6 alkylthio, C_1 - C_6
haloalkylthio, $R^{12}OC(O)N(R^{13})S-$, $R^{15}(R^{14})NS-$ and
10 benzyl optionally substituted with W;
 R^7 is selected from the group H, C_1 - C_6 alkyl, C_1 - C_6
haloalkyl and phenyl optionally substituted with
W;
 R^8 is selected from the group H, C_1 - C_3 alkyl,
15 CO_2R^{10} and $C(O)N(R^{10})R^{11}$;
 R^9 is selected from the group halogen, NO_2 , CN,
 C_1 - C_3 alkyl, C_1 - C_3 haloalkyl, OH, OR^{10} ,
 $S(O)_qR^{10}$, $N(H)R^{11}$, $N(R^{10})R^{11}$ and CO_2R^{10} ;
 R^{10} is selected from the group C_1 - C_4 alkyl, C_1 - C_4
20 haloalkyl, C_2 - C_4 alkenyl, C_2 - C_4 haloalkenyl,
 C_3 - C_4 alkynyl, C_3 - C_4 haloalkynyl, C_2 - C_6
alkoxyalkyl, C_2 - C_6 alkylthioalkyl, C_2 - C_6
cyanoalkyl, C_3 - C_6 alkoxycarbonyl alkyl, C_3 - C_6
cycloalkyl, C_3 - C_6 halocycloalkyl, C_4 - C_7
25 alkylcycloalkyl, C_4 - C_7 haloalkylcycloalkyl,
optionally substituted phenyl and optionally
substituted benzyl wherein the phenyl and benzyl
substituent(s) are 1 to 3 substituents
independently selected from W;
30 R^{11} is selected from the group H and C_1 - C_4 alkyl;
 R^{12} and R^{13} are independently selected from C_1 - C_6
alkyl;
 R^{14} and R^{15} are independently selected from C_1 - C_4
alkyl; or
35 R^{14} and R^{15} when attached to the same atom can be
taken together as $(CH_2)_5$ or $CH_2CH_2OCH_2CH_2$;

5 W is selected from the group halogen, CN, NO₂,
 C₁-C₂ alkyl, C₁-C₂ haloalkyl, C₁-C₂ alkoxy,
 C₁-C₂ haloalkoxy, C₁-C₃ alkylthio, C₁-C₂
 haloalkylthio, C₁-C₂ alkylsulfonyl, and C₁-C₂
 haloalkylsulfonyl;

10 m is 0 to 2;
 n is 1 to 2;
 p is 0 to 2; and
 q is 0 to 2.

15 In the above recitations, the term "alkyl", used
 either alone or in compound words such as "alkylthio" or
 haloalkyl", denotes straight chain or branched alkyl such
 as methyl, ethyl, n-propyl, isopropyl or the different
 butyl, pentyl, hexyl isomers. Alkoxy denotes methoxy,
20 ethoxy, n-propyloxy, isopropyloxy and the different
 butoxy, pentoxy or hexyloxy isomers. Alkenyl denotes
 straight chain or branched alkenes such as vinyl,
 1-propenyl, 2-propenyl, 2-propenyl and the different
 butenyl, pentenyl and hexenyl isomers. Alkynyl denotes
25 straight chain or branched alkynes such as ethynyl,
 1-propynyl, 3-propynyl and the different butynyl,
 pentynyl and hexynyl isomers. Alkylthio denotes
 methylthio, ethylthio and the different propylthio,
 butylthio, pentylthio and hexylthio isomers.
30 Alkylsulfinyl, alkylsulfonyl, alkylamino, and the like,
 are defined analogously to the above examples.
 Cycloalkyl denotes cyclopropyl, cyclobutyl, cyclopentyl
 and cyclohexyl.

 The term "halogen", either alone or in compound
35 words such as "haloalkyl", denotes fluorine, chlorine,
 bromine or iodine. Further, when used in compound words
 such as "haloalkyl" said alkyl can be partially or fully

5 substituted with halogen atoms, which can be the same or different. Examples of haloalkyl include $\text{CH}_2\text{CH}_2\text{F}$, CF_2CF_3 and CH_2CHFCl . The terms "halocycloalkyl" haloalkenyl" and "haloalkynyl" are defined analogously to the term "haloalkyl".

10 The total number of carbon atoms in a substituent group is indicated by the " $\text{C}_i\text{-C}_j$ " prefix where i and j are numbers from 1 to 7. For example, $\text{C}_1\text{-C}_3$ alkylsulfonyl would designate methylsulfonyl through propylsulfonyl; C_2 alkoxyalkoxy designates OCH_2OCH_3 ; C_4 alkoxyalkoxy
15 designates the various isomers of an alkoxy group substituted with a second alkoxy group containing a total of 4 carbon atoms, examples including $\text{OCH}_2\text{OCH}_2\text{CH}_2\text{CH}_3$ and $\text{OCH}_2\text{CH}_2\text{OCH}_2\text{CH}_3$; C_2 cyanoalkyl designates CH_2CN and C_3 cyanoalkyl designates $\text{CH}_2\text{CH}_2\text{CN}$ and $\text{CH}(\text{CN})\text{CH}_3$; C_2
20 alkylcarbonyl designates $\text{C}(\text{O})\text{CH}_3$ and C_4 alkylcarbonyl includes $\text{C}(\text{O})\text{CH}_2\text{CH}_2\text{CH}_3$ and $\text{C}(\text{O})\text{CH}(\text{CH}_3)_2$; and as a final example, C_3 alkoxy carbonylalkyl designates $\text{CH}_2\text{CO}_2\text{CH}_3$ and C_4 alkoxy carbonylalkyl includes $\text{CH}_2\text{CH}_2\text{CO}_2\text{CH}_3$, $\text{CH}_2\text{CO}_2\text{CH}_2\text{CH}_3$ and $\text{CH}(\text{CH}_3)\text{CO}_2\text{CH}_3$.

25 Preferred compounds A are those compounds of Formula I wherein:

- A is selected from the group $\text{C}_1\text{-C}_3$ alkylene and $\text{C}_3\text{-C}_6$ cycloalkylene each of which is optionally substituted with 1 or 2 R^9 ;
- 30 Q is selected from the group CO_2R^{10} , phenyl optionally substituted with $(\text{R}^4)_p$, $\text{C}_1\text{-C}_6$ alkyl optionally substituted with R^9 and $\text{C}_3\text{-C}_6$ cycloalkyl optionally substituted with R^9 ;
- X is O;
- 35 R^1 , R^2 , R^3 and R^4 are independently selected from the group halogen, CN, R^{10} , OR^{10} , $\text{S}(\text{O})_q\text{R}^{10}$ and $\text{OSO}_2\text{R}^{10}$;

- 5 R^5 and R^6 are independently selected from the group
 H, C_1 - C_2 alkyl, C_2 - C_3 alkylcarbonyl and C_2 - C_3
 alkoxy carbonyl;
 R^7 is selected from the group H and CH_3 ;
 R^8 is H;
10 R^9 is selected from the group halogen, CN, C_1 - C_3
 alkyl, C_1 - C_3 haloalkyl, OR^{10} , $S(O)_qR^{10}$ and
 CO_2R^{10} ;
 R^{10} is selected from the group C_1 - C_3 alkyl and C_1 - C_3
 haloalkyl;
15 R^{11} is selected from the group H or CH_3 ;
 W is selected from the group halogen, CN, NO_2 ,
 C_1 - C_2 alkyl, C_1 - C_2 haloalkyl, C_1 - C_2 alkoxy,
 C_1 - C_2 haloalkoxy, C_1 - C_2 alkylthio, C_1 - C_2
 haloalkylthio, C_1 - C_2 alkylsulfonyl and C_1 - C_2
20 haloalkylsulfonyl;
 m is 0 or 1;
 n is 1 with R^1 in the para-position;
 p is 0 or 1; and
 q is 0 or 2.

25

- Preferred compounds B are those of Preferred A
 wherein J is J-1. Preferred compounds C are those of
 Preferred A wherein J is J-2. Preferred compounds D are
 those of Preferred A wherein J is J-3. Preferred
30 compounds E are those of Preferred A wherein J is J-4.
 Preferred compounds F are those of Preferred A wherein J
 is J-5. Preferred compounds G are those of Preferred A
 wherein J is J-6. Preferred compounds H are those
 compounds of Formula I wherein A is C_1 - C_2 alkylene
35 optionally substituted with 1 or 2 methyl groups.

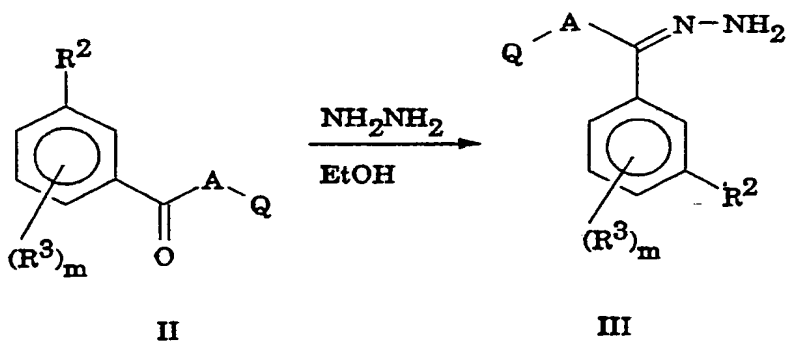
5 Specifically preferred for biological activity and ease of synthesis is the compound of Preferred B which is:

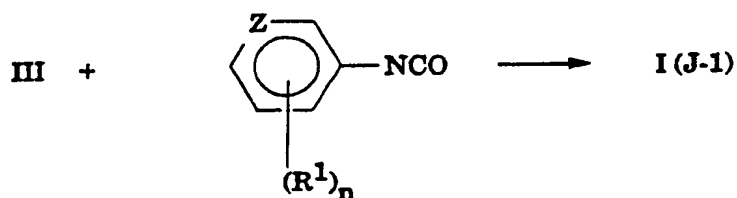
10 2-[2-phenyl-1-[3-(trifluoromethyl)phenyl]-ethylidene]-N-[4-(trifluoromethoxy)phenyl]-hydrazine carboxamide.

DETAILS OF THE INVENTION

Compounds of Formula I (J-1) can be prepared from ketones of Formula II by a two-step process whereby the Formula II compound is condensed with hydrazine and then
15 reacted with a suitably substituted aryl isocyanate of Formula IV. Procedures for the condensation of hydrazine with ketones are well known. For the purposes of this invention, combination of the Formula II ketone with 1 to 2 equivalents of hydrazine hydrate in an alcoholic
20 solvent such as methanol, ethanol or propanol at the reflux temperature of the solvent affords the intermediate hydrazones of Formula III. Subsequent reaction of the Formula III hydrazone with an equimolar amount of an aryl isocyanate affords the Formula I
25 semicarbazones, typically as high melting solids.

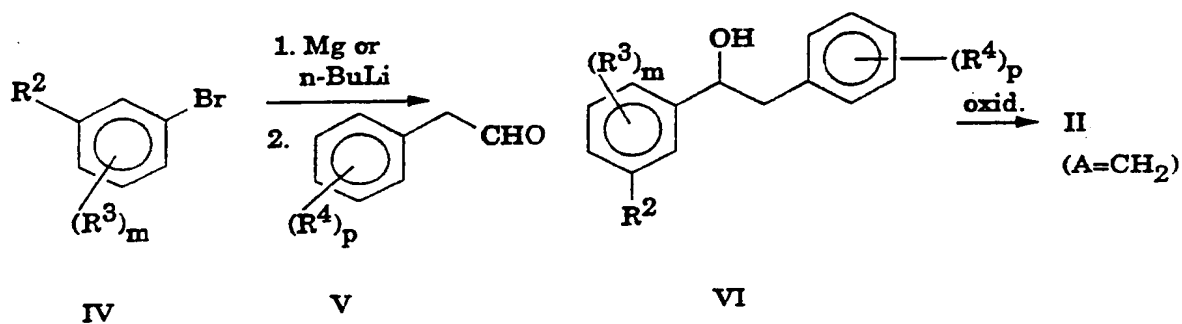
SCHEME 1



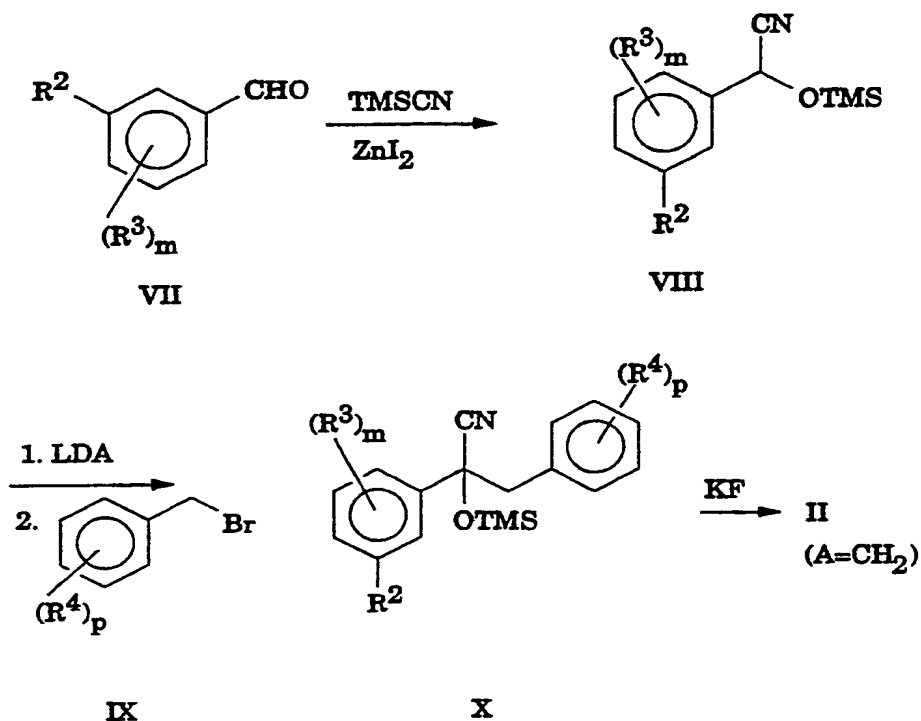


Ketones of Formula II are either known in the art or are available via procedures analogous to known ones. For example, addition of an aryl magnesium or aryl lithium derivative to an optionally substituted phenyl acetaldehyde affords an intermediate alcohol VI which is then readily oxidized to the Formula II ketone (Scheme 2). Alternatively, alkylation of a trimethylsilylcyano-
hydrin (Formula VIII) with a benzyl halide followed by
conversion of the trimethylsilylcyanohydrin group to the
ketone is a useful method for synthesis of the Formula II
compounds (Scheme 3).

SCHEME 2



5

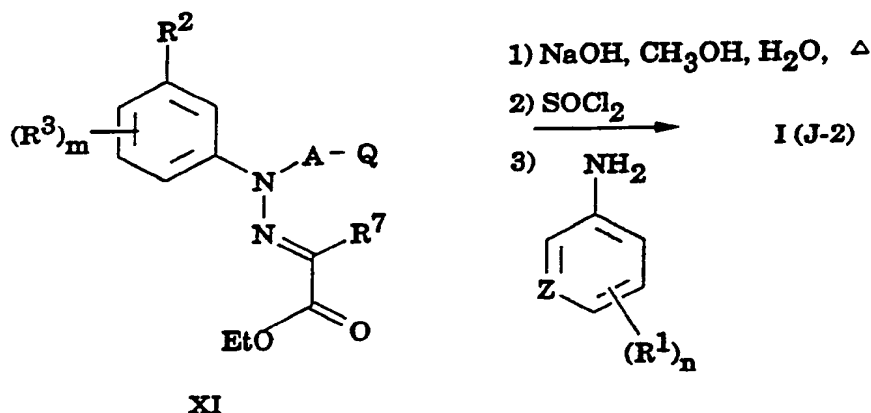
SCHEME 3

10

Compounds of the Formula I (J-2) can be prepared in a conventional three-step process whereby Formula XI esters are saponified, converted to the acid chloride and reacted with an appropriately substituted aniline or pyridine. Scheme 3A illustrates this method.

15

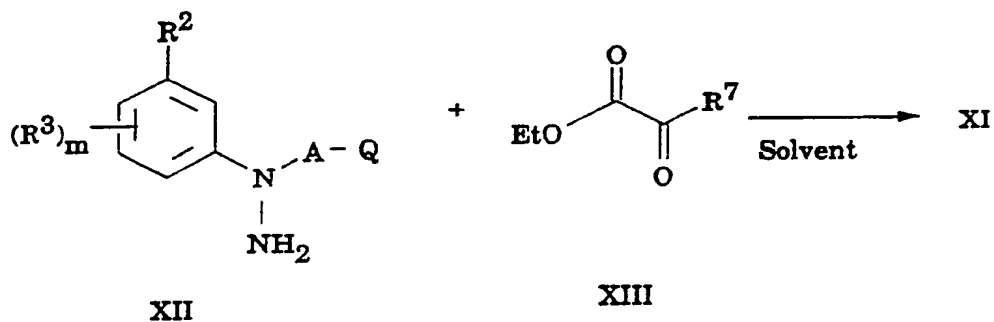
5

SCHEME 3A

Formula XI compounds can be prepared by the reaction of Formula XII hydrazines with esters of the Formula XIII. The reaction can be conducted in the presence or the absence of an acid or base in an unreactive solvent system such as methanol, ethanol, methylene chloride, chloroform, tetrahydrofuran and dioxane, but not limited to these. The temperature of the reaction can be varied from 0°C to the reflux temperature of the particular solvent. The reaction is usually complete in 24 h. Scheme 4 illustrates this transformation.

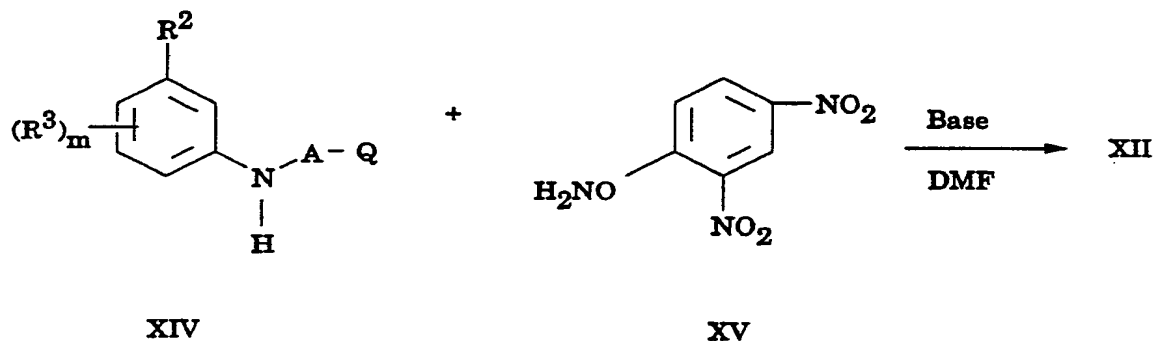
SCHEME 4

20



5 Compounds of the Formula XII can be prepared by the
reaction of Formula XIV derivatives with the reagent
O-(2,4-dinitrophenyl)hydroxylamine (XV) in the presence
of a base such as sodium carbonate, sodium bicarbonate or
potassium carbonate in a nonreactive solvent such as, but
10 not limited to, dimethylformamide, dimethylsulfoxide,
tetrahydrofuran and dioxane. The reaction temperature
can vary from 0°C to 100°C with 25°C being preferred.
The reaction is usually complete in 24 h. This procedure
is analogous to that described in J. Med. Chem., 1984,
15 27, 1103. Scheme 5 illustrates these transformations.

SCHEME 5

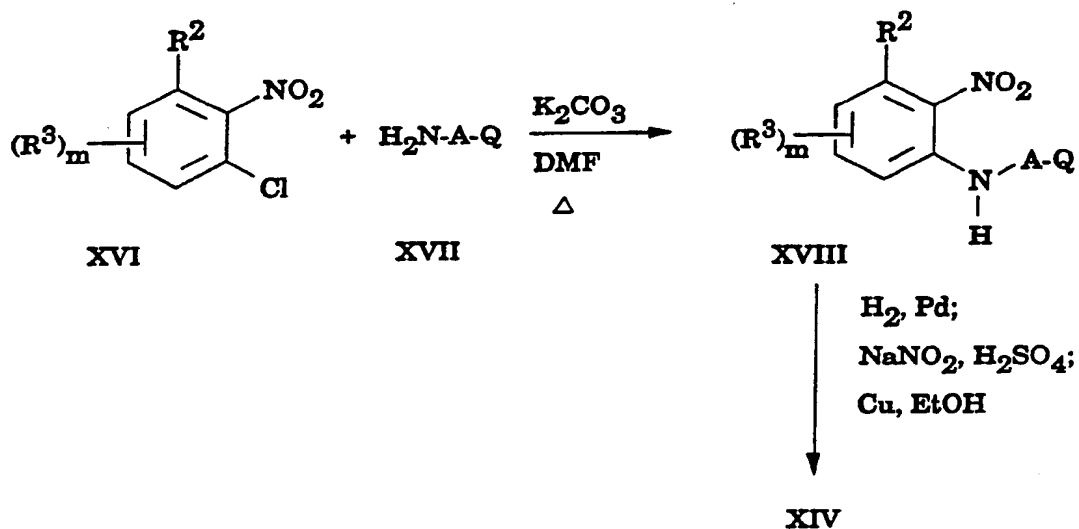


20

Compounds of the Formula XIV can be prepared by a
two-step process whereby Formula XVI compounds are
reacted with appropriately-substituted amines of Formula
XVI in the presence of a base such as sodium- or
25 potassium carbonate in a solvent such as
dimethylformamide, dimethylsulfoxide, tetrahydrofuran and
the like. The temperature of the reaction can vary from
about 25°C to 150°C and the reaction is usually complete
in 48 h. In the subsequent step, the ortho-nitro
30 substituent can be removed by hydrogenation and reductive
diazotization (Tetrahedron Lett. 1989, 929). For further

5 references on this transformation see March, Advanced Org. Chem., 1985, 646. Scheme 6 illustrates these transformations.

SCHEME 6



10

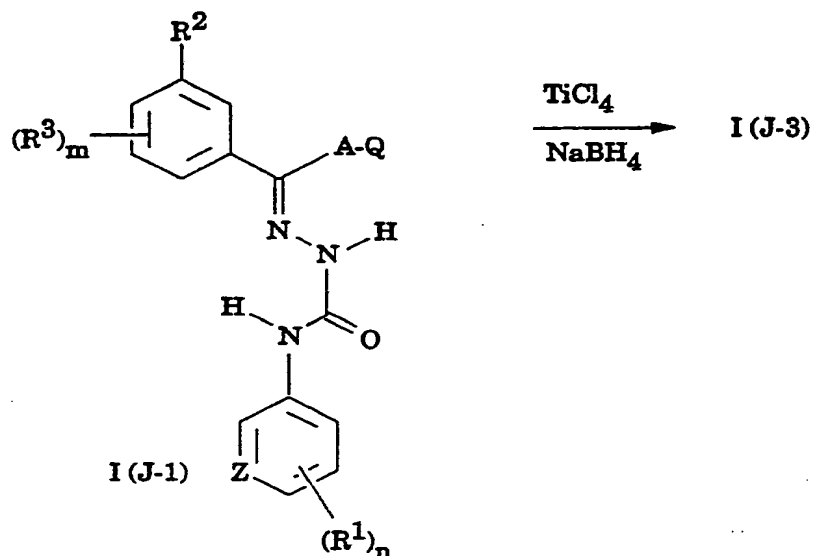
One skilled in the art will recognize Formula XVII compounds as substituted amines of which the preparations are well documented in the literature (J. Chem. Soc.,
15 Chem. Commun. 1987, 897; Synth. Commun. 1980, 10, 107).

Compounds of Formula I (J-3) can be prepared by the reaction of tri- and tetravalent metal species such as titanium, silicon, tin and the like in combination with a reducing agent such as sodium, lithium, or zinc
20 borohydride, lithium aluminum hydride and the like with compounds of Formula I (J-1) as illustrated in Scheme 7. Literature disclosure of analogous reactions can be found in J. Org. Chem., 1987, 54, 3750, and Synthesis, 1980, 695. Typical reactions involve the addition of 1
25 equivalent of a compound of Formula I (J-1) to a solution of 1.1 to 4 equivalents of titanium tetrachloride, with

5 1.5 to 2.5 equivalents being preferred, and 2.1 to 6 equivalents of sodium borohydride with 3.5-4.5 equivalents being preferred.

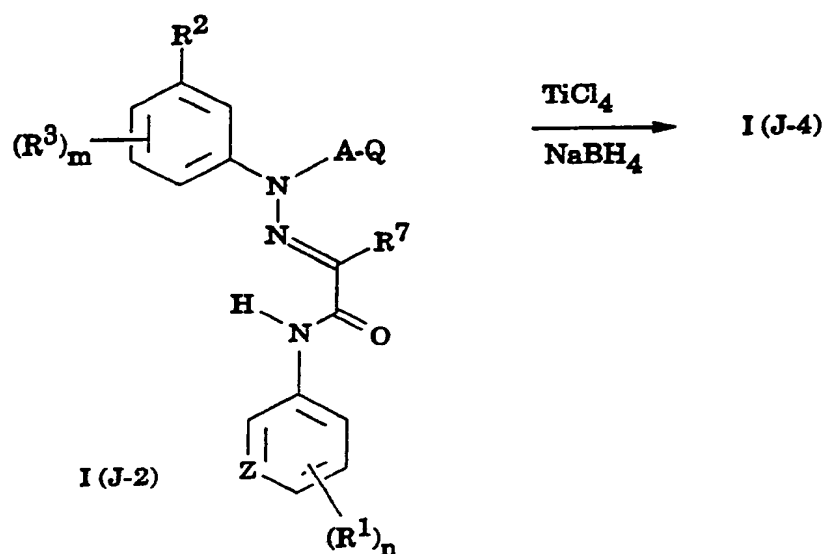
Conventional organic solvents such as ether, tetrahydrofuran, dimethoxyethane, methylene chloride and
 10 chloroform can be used with 1,2-dimethoxyethane being preferred. The reaction can be conducted at temperatures ranging from -70°C to 50°C with -10°C to 30°C being preferred. The reaction time can be 0.1 hour to 48 hours with 2 to 4 hours being preferred.

15

SCHEME 7

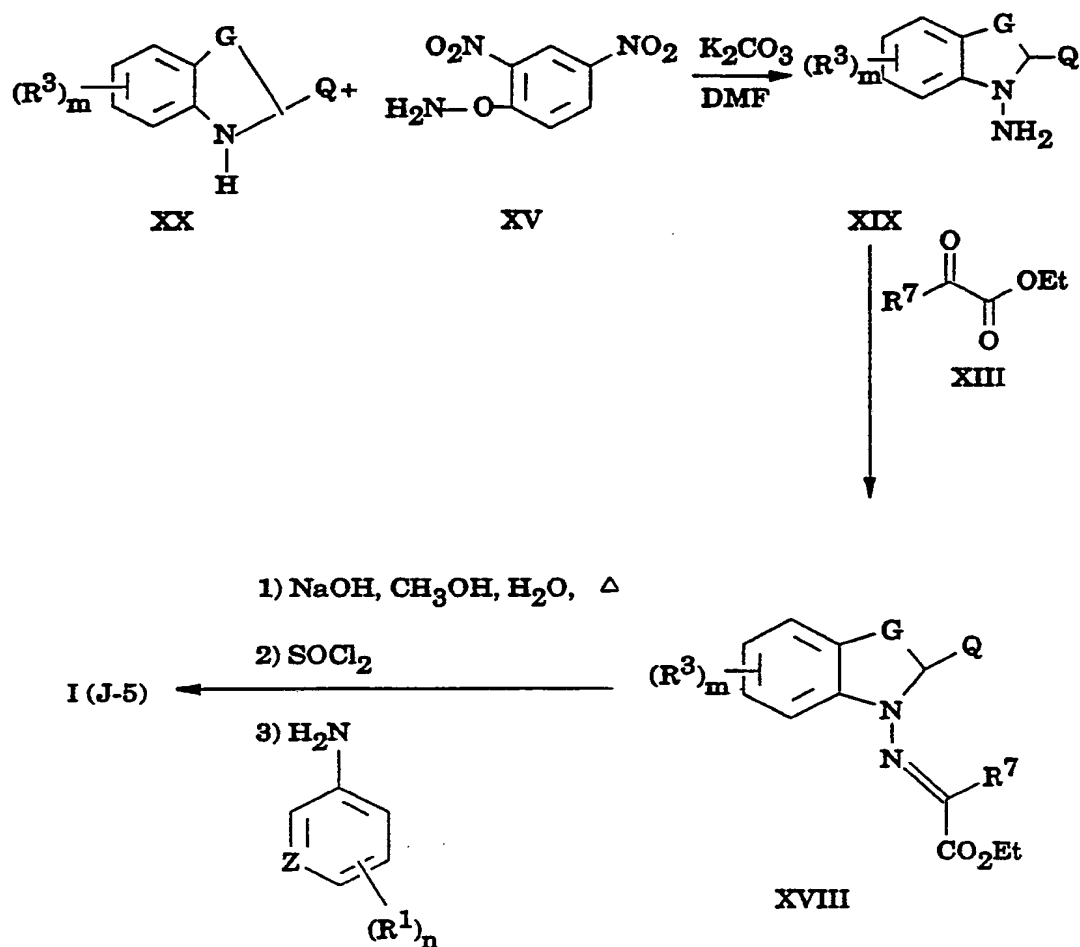
Compounds of the Formula I (J-4) can be prepared
 20 from Formula I (J-2) derivatives in an analogous fashion as that described for Formula I (J-3) compounds. Scheme 8 illustrates this method.

5

SCHEME 8

Compounds of the Formula I (J-5) can be prepared in
10 an analogous fashion as described for the preparation of
Formula I (J-2) derivatives. Scheme 9 illustrates these
transformations.

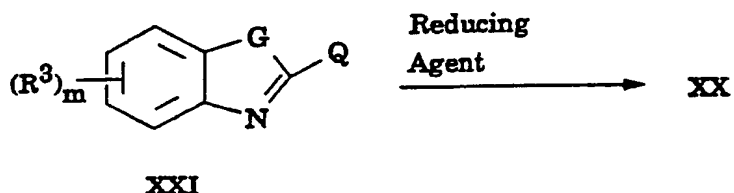
SCHEME 9



Formula XX compounds can be prepared by the reaction of Formula XXI derivatives with metal hydride reducing agents such as zinc borohydride, lithium borohydride, sodium borohydride, lithium aluminum hydride and the like in conventional organic solvents such as ether, tetrahydrofuran, dimethoxyethane and dioxane. The reaction can be conducted at temperatures from $-78^\circ C$ to the reflux temperature of the particular solvent. The

5 reaction is usually complete in 48 h. Scheme 10 illustrates this method.

SCHEME 10



10

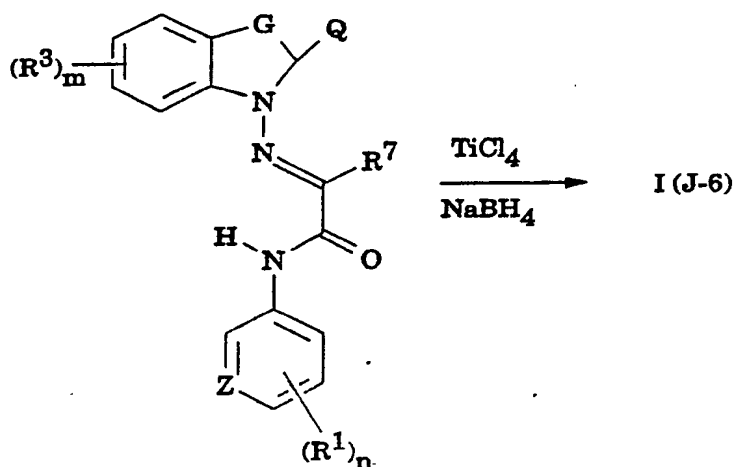
One skilled in the art will recognize Formula XXI derivatives to be indoles and dihydroquinolines of which the preparations are well documented in the literature (J. Med. Chem., 1984, 1439).

15

Compounds of the Formula I (J-6) can be prepared from Formula I (J-5) derivatives by an analogous procedure as described for Formula I (J-3) compounds. Scheme 11 illustrates this method.

SCHEME 11

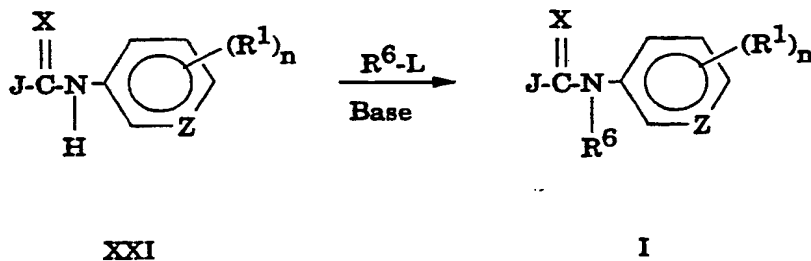
20



Compounds of Formula I, where R⁶ is other than H, can be prepared from compounds of Formula XXI (i.e.,

5 compounds of Formula I where R^6 is H) by the reaction
with electrophiles R^6-L (where L is a leaving group such
as Cl, Br, I, alkylsulfonate or arylsulfonate). Useful
electrophiles include alkyl halides, such as methyl
10 iodide, dialkylsulfates, such as dimethylsulfate, acyl
halides, such as acetyl chloride and alkylchloroformates,
such as ethyl chloroformate. The reaction is typically
run in polar organic solvents such as tetrahydrofuran and
dimethylformamide, and in the presence of a strong base,
examples of which include sodium hydride, potassium
15 hydride and potassium t-butoxide. For compounds of
Formula XXI containing more than one free NH group,
protecting groups may be required to achieve the desired
N-substitution. This reaction is illustrated in Scheme
12.

20

SCHEME 12

The following Example illustrates the invention.

5

EXAMPLE 1

[1-(3-Chlorophenyl)-2-phenylethylidenel-N-[4-(tri-
fluoromethyl)phenyl]hydrazinecarboxamide

Step A: 2-Phenyl-1-(3-chlorophenyl)ethanone

To a solution of 3-bromochlorobenzene (15 g, 78.3
10 mmol) in 150 ml of dry tetrahydrofuran was added 2.5 M
n-butyllithium in hexane (31.4 ml, 78.3 mmol) dropwise at
-78°C. A white precipitate crystallized out of the
reaction mixture. The reaction was warmed to -20°C at
which point the precipitate went into solution. To the
15 reaction was then added phenylacetaldehyde (9.4 g, 78.3
mmol) in 30 ml of dry tetrahydrofuran at -25°C. The
reaction was then gradually warmed to room temperature
and partitioned between ether and 5% aqueous sodium
bicarbonate. The ether extracts were then dried over
20 magnesium sulfate and concentrated to 18.86 g of a yellow
oil which was purified by chromatography on silica gel
(2.5% ethyl acetate in hexane) to afford 10.68 g of a
yellow oil, which was confirmed by proton NMR to be
1-(3-chlorophenyl)benzeneethanol.

25 To a solution of 1-(3-chlorophenyl)benzeneethanol
(9.44 g, 40.6 mmol) in 150 ml of methylene chloride was
added pyridinium chlorochromate (13.1 g, 60.9 mmol) and
the mixture was stirred under nitrogen overnight. After
this time, the reaction was diluted with 250 ml of ether,
30 filtered through magnesium sulfate and concentrated to
9.34 g of a brown oil. Chromatography on silica gel (10%
ethyl acetate in hexane) afforded 8.23 g of the title
compound as a yellow solid.

¹H NMR (CDCl₃): δ 4.25 (s, 2H), 7.2-7.6 (m, 7H), 7.85
35 (d, 1H), 7.97 (s, 1H).

5

Step B: [1-(3-chlorophenyl-2-phenylethylidene)-
N-[4-(trifluoromethyl)phenyl]hydrazine-
carboxamide

To a solution of the ketone from Step A (2.0 g, 8.7
10 mmol) in 20 ml of ethanol was added hydrazine hydrate
(0.51 ml, 10.4 mmol) and the mixture was heated at reflux
under nitrogen overnight. The reaction was then
concentrated and partitioned between ether and 5% aqueous
sodium bicarbonate. The ether extracts were washed with
15 water, dried over magnesium sulfate and concentrated to
1.86 g of a dark yellow oil. To a mixture of 0.93 g of
this oil (3.8 mmol) in 15 ml of tetrahydrofuran was added
4-trifluoromethylphenylisocyanate (0.71 g, 3.8 mmol) and
the reaction was stirred under nitrogen for 72 hours.
20 The reaction was then concentrated and the residue
trituated with ether to afford 0.87 g of the title
compound as a white solid, mp 225-229°C.
¹H NMR (CDCl₃): δ 4.05 (s, 2H), 7.1-7.5 (m, 7H), 7.55
(d, 2H), 7.65 (d, 2H), 7.78 (bs, 1H), 8.08 (s, 1H), 8.42
25 (s, 1H).

By the general procedures described herein, or
obvious modifications thereof, the compounds of Tables 1
through 12 can be prepared. In the Table Key, nPr is
30 n-propyl, iPr is isopropyl and cPr is cyclopropyl.

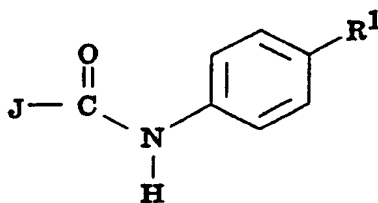
KEY FOR TABLES 1 TO 12

Table	Group	J
1 (a)	a	J-1 (A=CH ₂ , Q=Me, R ⁵ =H)
1 (a)	b	J-1 (A=CH ₂ , Q=nPr, R ⁵ =H)
1 (a)	c	J-1 (A=CH ₂ , Q=iPr, R ⁵ =H)
2 (b)	a	J-1 (A=CH ₂ , Q=CO ₂ Me, R ⁵ =H)
2 (b)	b	J-1 (A=CH ₂ , Q=Ph, R ⁵ =H)
2 (b)	c	J-1 (A=CH ₂ , Q=4-F-Ph, R ⁵ =H)
2 (b)	d	J-1 (A=CH ₂ , Q=4-Cl-Ph, R ⁵ =H)
2 (b)	e	J-1 (A=CH ₂ , Q=4-CF ₃ -Ph, R ⁵ =H)
2 (b)	f	J-1 (A=CH ₂ , Q=4-OCF ₂ H-Ph, R ⁵ =H)
2 (b)	g	J-1 (A=CH ₂ , Q=4-OCF ₃ -Ph, R ⁵ =H)
2 (b)	h	J-1 (A=CH ₂ , Q=4-Me-Ph, R ⁵ =H)
2 (b)	i	J-1 (A=cPr, Q=Me, R ⁵ =H)
2 (b)	j	J-1 (A=cPr, Q=nPr, R ⁵ =H)
2 (b)	k	J-1 (A=cPr, Q=iPr, R ⁵ =H)
2 (b)	l	J-1 (A=cPr, Q=CO ₂ Me, R ⁵ =H)
2 (b)	m	J-1 (A=cPr, Q=Ph, R ⁵ =H)
2 (b)	n	J-1 (A=cPr, Q=4-F-Ph, R ⁵ =H)
2 (b)	o	J-1 (A=cPr, Q=4-Cl-Ph, R ⁵ =H)

Table	Group	J
2 (b)	p	J-1 (A=cPr, Q=4-CF ₃ -Ph, R ⁵ =H)
2 (b)	q	J-1 (A=cPr, Q=4-OCF ₂ H-Ph, R ⁵ =H)
2 (b)	r	J-1 (A=cPr, Q=4-OCF ₃ -Ph, R ⁵ =H)
2 (b)	s	J-1 (A=cPr, Q=4-Me-Ph, R ⁵ =H)
3 (c)	a	J-2 (A=CH ₂ , Q=Me, R ³ =H)
3 (c)	b	J-2 (A=CH ₂ , Q=nPr, R ³ =H)
3 (c)	c	J-2 (A=CH ₂ , Q=iPr, R ³ =H)
3 (c)	d	J-2 (A=CH ₂ , Q=CO ₂ Me, R ³ =H)
3 (c)	e	J-2 (A=CH ₂ , Q=Ph, R ³ =H)
3 (c)	f	J-2 (A=CH ₂ , Q=4-F-Ph, R ³ =H)
3 (c)	g	J-2 (A=CH ₂ , Q=4-Cl-Ph, R ³ =H)
3 (c)	h	J-2 (A=cPr, Q=Me, R ³ =H)
3 (c)	i	J-2 (A=cPr, Q=nPr, R ³ =H)
3 (c)	j	J-2 (A=cPr, Q=iPr, R ³ =H)
3 (c)	k	J-2 (A=cPr, Q=CO ₂ Me, R ³ =H)
3 (c)	l	J-2 (A=cPr, Q=Ph, R ³ =H)
3 (c)	m	J-2 (A=cPr, Q=4-F-Ph, R ³ =H)
3 (c)	n	J-2 (A=cPr, Q=4-Cl-Ph, R ³ =H)
4 (d)	a	J-3 (A=CH ₂ , Q=Me, R ³ =H, R ⁵ =H)
4 (d)	b	J-3 (A=CH ₂ , Q=nPr, R ³ =H, R ⁵ =H)
4 (d)	c	J-3 (A=CH ₂ , Q=iPr, R ³ =H, R ⁵ =H)
4 (d)	d	J-3 (A=CH ₂ , Q=CO ₂ Me, R ³ =H, R ⁵ =H)
4 (d)	e	J-3 (A=CH ₂ , Q=Ph, R ³ =H, R ⁵ =H)
4 (d)	f	J-3 (A=CH ₂ , Q=4-F-Ph, R ³ =H, R ⁵ =H)
4 (d)	g	J-3 (A=CH ₂ , Q=4-Cl-Ph, R ³ =H, R ⁵ =H)
4 (d)	h	J-3 (A=cPr, Q=Me, R ³ =H, R ⁵ =H)
4 (d)	i	J-3 (A=cPr, Q=nPr, R ³ =H, R ⁵ =H)
4 (d)	j	J-3 (A=cPr, Q=iPr, R ³ =H, R ⁵ =H)
4 (d)	k	J-3 (A=cPr, Q=CO ₂ Me, R ³ =H, R ⁵ =H)
4 (d)	l	J-3 (A=cPr, Q=Ph, R ³ =H, R ⁵ =H)
4 (d)	m	J-3 (A=cPr, Q=4-F-Ph, R ³ =H, R ⁵ =H)

Table	Group	J
4 (d)	n	J-3 (A=cPr, Q=4-Cl-Ph, R ³ =H, R ⁵ =H)
5 (e)	a	J-4 (A=CH ₂ , Q=Me, R ³ =H, R ⁸ =H)
5 (e)	b	J-4 (A=CH ₂ , Q=nPr, R ³ =H, R ⁸ =H)
5 (e)	c	J-4 (A=CH ₂ , Q=iPr, R ³ =H, R ⁸ =H)
5 (e)	d	J-4 (A=CH ₂ , Q=CO ₂ Me, R ³ =H, R ⁸ =H)
5 (e)	e	J-4 (A=CH ₂ , Q=Ph, R ³ =H, R ⁸ =H)
5 (e)	f	J-4 (A=CH ₂ , Q=4-F-Ph, R ³ =H, R ⁸ =H)
5 (e)	g	J-4 (A=CH ₂ , Q=4-Cl-Ph, R ³ =H, R ⁸ =H)
5 (e)	h	J-4 (A=cPr, Q=Me, R ³ =H, R ⁸ =H)
5 (e)	i	J-4 (A=cPr, Q=nPr, R ³ =H, R ⁸ =H)
5 (e)	j	J-4 (A=cPr, Q=iPr, R ³ =H, R ⁸ =H)
5 (e)	k	J-4 (A=cPr, Q=CO ₂ Me, R ³ =H, R ⁸ =H)
5 (e)	l	J-4 (A=cPr, Q=Ph, R ³ =H, R ⁸ =H)
5 (e)	m	J-4 (A=cPr, Q=4-F-Ph, R ³ =H, R ⁸ =H)
5 (e)	n	J-4 (A=cPr, Q=4-Cl-Ph, R ³ =H, R ⁸ =H)
6 (f)	a	J-5 (G=CH ₂ , Q=Me)
6 (f)	b	J-5 (G=CH ₂ , Q=nPr)
6 (f)	c	J-5 (G=CH ₂ , Q=iPr)
6 (f)	d	J-5 (G=CH ₂ , Q=CO ₂ Me)
6 (f)	e	J-5 (G=CH ₂ , Q=Ph)
6 (f)	f	J-5 (G=CH ₂ , Q=4-F-Ph)
6 (f)	g	J-5 (G=CH ₂ , Q=4-Cl-Ph)
6 (f)	h	J-5 (G=CH ₂ CH ₂ , Q=Me)
6 (f)	i	J-5 (G=CH ₂ CH ₂ , Q=nPr)
6 (f)	j	J-5 (G=CH ₂ CH ₂ , Q=iPr)
6 (f)	k	J-5 (G=CH ₂ CH ₂ , Q=CO ₂ Me)
6 (f)	l	J-5 (G=CH ₂ CH ₂ , Q=Ph)
6 (f)	m	J-5 (G=CH ₂ CH ₂ , Q=4-F-Ph)
6 (f)	n	J-5 (G=CH ₂ CH ₂ , Q=4-Cl-Ph)
7 (g)	a	J-6 (G=CH ₂ , Q=Me, R ⁸ =H)
7 (g)	b	J-6 (G=CH ₂ , Q=nPr, R ⁸ =H)

Table	Group	J
7 (g)	c	J-6 (G=CH ₂ , Q=iPr, R ⁸ =H)
7 (g)	d	J-6 (G=CH ₂ , Q=CO ₂ Me, R ⁸ =H)
7 (g)	e	J-6 (G=CH ₂ , Q=Ph, R ⁸ =H)
7 (g)	f	J-6 (G=CH ₂ , Q=4-F-Ph, R ⁸ =H)
7 (g)	g	J-6 (G=CH ₂ , Q=4-Cl-Ph, R ⁸ =H)
7 (g)	h	J-6 (G=CH ₂ CH ₂ , Q=Me, R ⁸ =H)
7 (g)	i	J-6 (G=CH ₂ CH ₂ , Q=nPr, R ⁸ =H)
7 (g)	j	J-6 (G=CH ₂ CH ₂ , Q=iPr, R ⁸ =H)
7 (g)	k	J-6 (G=CH ₂ CH ₂ , Q=CO ₂ Me, R ⁸ =H)
7 (g)	l	J-6 (G=CH ₂ CH ₂ , Q=Ph, R ⁸ =H)
7 (g)	m	J-6 (G=CH ₂ CH ₂ , Q=4-F-Ph, R ⁸ =H)
7 (g)	n	J-6 (G=CH ₂ CH ₂ , Q=4-Cl-Ph, R ⁸ =H)
8 (h)	a	J-1 (A=CH ₂ , Q=Me, R ⁵ =Me)
8 (h)	b	J-1 (A=CH ₂ , Q=nPr, R ⁵ =Me)
8 (h)	c	J-1 (A=CH ₂ , Q=iPr, R ⁵ =Me)
9 (i)	a	J-1 (A=CH ₂ , Q=CO ₂ Me, R ⁵ =Me)
9 (i)	b	J-1 (A=CH ₂ , Q=Ph, R ⁵ =Me)
9 (i)	c	J-1 (A=CH ₂ , Q=4-F-Ph, R ⁵ =Me)
9 (i)	d	J-1 (A=CH ₂ , Q=4-Cl-Ph, R ⁵ =Me)
9 (i)	e	J-1 (A=CH ₂ , Q=4-CF ₃ -Ph, R ⁵ =Me)
9 (i)	f	J-1 (A=CH ₂ , Q=4-OCF ₂ H-Ph, R ⁵ =Me)
9 (i)	g	J-1 (A=CH ₂ , Q=4-OCF ₃ -Ph, R ⁵ =Me)
9 (i)	h	J-1 (A=CH ₂ , Q=4-Me-Ph, R ⁵ =Me)
9 (i)	i	J-1 (A=cPr, Q=Me, R ⁵ =Me)
9 (i)	j	J-1 (A=cPr, Q=nPr, R ⁵ =Me)
9 (i)	k	J-1 (A=cPr, Q=iPr, R ⁵ =Me)
9 (i)	l	J-1 (A=cPr, Q=CO ₂ Me, R ⁵ =Me)
9 (i)	m	J-1 (A=cPr, Q=Ph, R ⁵ =Me)
9 (i)	n	J-1 (A=cPr, Q=4-F-Ph, R ⁵ =Me)
9 (i)	o	J-1 (A=cPr, Q=4-Cl-Ph, R ⁵ =Me)
9 (i)	p	J-1 (A=cPr, Q=4-CF ₃ -Ph, R ⁵ =Me)

Table	Group	J
9(i)	q	J-1 (A=cPr, Q=4-OCF ₂ H-Ph, R ⁵ =Me)
9(i)	r	J-1 (A=cPr, Q=4-OCF ₃ -Ph, R ⁵ =Me)
9(i)	s	J-1 (A=cPr, Q=4-Me-Ph, R ⁵ =Me)
10(j)	a	J-1 (A=CH ₂ , Q=Me, R ⁵ =CO ₂ Me)
10(j)	b	J-1 (A=CH ₂ , Q=nPr, R ⁵ =CO ₂ Me)
10(j)	c	J-1 (A=CH ₂ , Q=iPr, R ⁵ =CO ₂ Me)
11(k)	a	J-1 (A=CH ₂ , Q=CO ₂ Me, R ⁵ =CO ₂ Me)
11(k)	b	J-1 (A=CH ₂ , Q=Ph, R ⁵ =CO ₂ Me)
11(k)	c	J-1 (A=CH ₂ , Q=4-F-Ph, R ⁵ =CO ₂ Me)
11(k)	d	J-1 (A=CH ₂ , Q=4-Cl-Ph, R ⁵ =CO ₂ Me)
11(k)	e	J-1 (A=CH ₂ , Q=4-CF ₃ -Ph, R ⁵ =CO ₂ Me)
11(k)	f	J-1 (A=CH ₂ , Q=4-OCF ₂ H-Ph, R ⁵ =CO ₂ Me)
11(k)	g	J-1 (A=CH ₂ , Q=4-OCF ₃ -Ph, R ⁵ =CO ₂ Me)
11(k)	h	J-1 (A=CH ₂ , Q=4-Me-Ph, R ⁵ =CO ₂ Me)
11(k)	i	J-1 (A=cPr, Q=Me, R ⁵ =CO ₂ Me)
11(k)	j	J-1 (A=cPr, Q=nPr, R ⁵ =CO ₂ Me)
11(k)	k	J-1 (A=cPr, Q=iPr, R ⁵ =CO ₂ Me)
11(k)	l	J-1 (A=cPr, Q=CO ₂ Me, R ⁵ =CO ₂ Me)
11(k)	m	J-1 (A=cPr, Q=Ph, R ⁵ =CO ₂ Me)
11(k)	n	J-1 (A=cPr, Q=4-F-Ph, R ⁵ =CO ₂ Me)
11(k)	o	J-1 (A=cPr, Q=4-Cl-Ph, R ⁵ =CO ₂ Me)
11(k)	p	J-1 (A=cPr, Q=4-CF ₃ -Ph, R ⁵ =CO ₂ Me)
11(k)	q	J-1 (A=cPr, Q=4-OCF ₂ H-Ph, R ⁵ =CO ₂ Me)
11(k)	r	J-1 (A=cPr, Q=4-OCF ₃ -Ph, R ⁵ =CO ₂ Me)
11(k)	s	J-1 (A=cPr, Q=4-Me-Ph, R ⁵ =CO ₂ Me)
12(l)	a	J-1 (A=CH ₂ , Q=CO ₂ Me, R ⁵ =H, R ⁶ =Me)
12(l)	b	J-1 (A=CH ₂ , Q=Ph, R ⁵ =H, R ⁶ =Me)
12(l)	c	J-1 (A=CH ₂ , Q=4-F-Ph, R ⁵ =H, R ⁶ =Me)
12(l)	d	J-1 (A=CH ₂ , Q=4-Cl-Ph, R ⁵ =H, R ⁶ =Me)
12(l)	e	J-1 (A=CH ₂ , Q=4-CF ₃ -Ph, R ⁵ =H, R ⁶ =Me)
12(l)	f	J-1 (A=CH ₂ , Q=4-OCF ₂ H-Ph, R ⁵ =H, R ⁶ =Me)

Table	Group	J
12 (1)	g	J-1 (A=CH ₂ , Q=4-OCF ₃ -Ph, R ⁵ =H, R ⁶ =Me)
12 (1)	h	J-1 (A=CH ₂ , Q=4-Me-Ph, R ⁵ =H, R ⁶ =Me)
12 (1)	i	J-1 (A=cPr, Q=Me, R ⁵ =H, R ⁶ =Et)
12 (1)	j	J-1 (A=cPr, Q=nPr, R ⁵ =H, R ⁶ =Et)
12 (1)	k	J-1 (A=cPr, Q=iPr, R ⁵ =H, R ⁶ =Et)
12 (1)	l	J-1 (A=cPr, Q=CO ₂ Me, R ⁵ =H, R ⁶ =Et)
12 (1)	m	J-1 (A=cPr, Q=Ph, R ⁵ =H, R ⁶ =Et)
12 (1)	n	J-1 (A=cPr, Q=4-F-Ph, R ⁵ =H, R ⁶ =Et)
12 (1)	o	J-1 (A=cPr, Q=4-Cl-Ph, R ⁵ =H, R ⁶ =Me)
12 (1)	p	J-1 (A=cPr, Q=4-CF ₃ -Ph, R ⁵ =H, R ⁶ =Et)
12 (1)	q	J-1 (A=cPr, Q=4-OCF ₂ H-Ph, R ⁵ =H, R ⁶ =Et)
12 (1)	r	J-1 (A=cPr, Q=4-OCF ₃ -Ph, R ⁵ =H, R ⁶ =Et)
12 (1)	s	J-1 (A=cPr, Q=4-Me-Ph, R ⁵ =H, R ⁶ =Et)

- (a) Compounds of Table 1 wherein R¹, R² and R³ are as set out therein can be prepared having the recited values of groups a through c.
- (b) Compounds of Table 2 wherein R¹, R² and R³ are as set out therein can be prepared having the recited values of groups a through s.
- (c) Compounds of Table 3 wherein R¹, R² and R⁷ are as set out therein can be prepared having the recited values of groups a through n.
- (d) Compounds of Table 4 wherein R¹, R² and R⁸ are as set out therein can be prepared having the recited values of groups a through n.
- (e) Compounds of Table 5 wherein R¹, R² and R⁷ are as set out therein can be prepared having the recited values of groups a through n.

- (f) Compounds of Table 6 wherein R^1 , R^3 and R^7 are as set out therein can be prepared having the recited values of groups a through n.
- (g) Compounds of Table 7 wherein R^1 , R^3 and R^7 are as set out therein can be prepared having the recited values of groups a through n.
- (h) Compounds of Table 8 wherein R^1 , R^2 and R^3 are as set out therein can be prepared having the recited values of groups a through c.
- (i) Compounds of Table 9 wherein R^1 , R^2 and R^3 are as set out therein can be prepared having the recited values of groups a through s.
- (j) Compounds of Table 10 wherein R^1 , R^2 and R^3 are as set out therein can be prepared having the recited values of groups a through c.
- (k) Compounds of Table 11 wherein R^1 , R^2 and R^3 are as set out therein can be prepared having the recited values of groups a through s.
- (l) Compounds of Table 12 wherein R^1 , R^2 and R^3 are as set out therein can be prepared having the recited values of groups a through s.

TABLE 1

R ¹	R ²	R ³	R ¹	R ²	R ³
Br	Cl	H	Br	OCH ₂ CF ₃	H
CF ₃	Cl	H	CF ₃	OCH ₂ CF ₃	H
OCF ₃	Cl	H	OCF ₃	OCH ₂ CF ₃	H
OCF ₂ H	Cl	H	OCF ₂ H	OCH ₂ CF ₃	H
OSO ₂ CF ₃	Cl	H	OSO ₂ CF ₃	OCH ₂ CF ₃	H
Br	Br	H	Br	OCF ₂ H	H
CF ₃	Br	H	CF ₃	OCF ₂ H	H
OCF ₃	Br	H	OCF ₃	OCF ₂ H	H
OCF ₂ H	Br	H	OCF ₂ H	OCF ₂ H	H
OSO ₂ CF ₃	Br	H	OSO ₂ CF ₃	OCF ₂ H	H
Br	CF ₃	H	Br	CN	H
CF ₃	CF ₃	H	CF ₃	CN	H
OCF ₃	CF ₃	H	OCF ₃	CN	H
OCF ₂ H	CF ₃	H	OCF ₂ H	CN	H
OSO ₂ CF ₃	CF ₃	H	OSO ₂ CF ₃	CN	H
Br	F	H	Br	OCH ₃	H
CF ₃	F	H	CF ₃	OCH ₃	H
OCF ₃	F	H	OCF ₃	OCH ₃	H
OCF ₂ H	F	H	OCF ₂ H	OCH ₃	H
OSO ₂ CF ₃	F	H	OSO ₂ CF ₃	OCH ₃	H

TABLE 2

R ¹	R ²	R ³	R ¹	R ²	R ³
Cl	Cl	H	Cl	OCH ₂ CF ₃	H
Br	Cl	H	Br	OCH ₂ CF ₃	H
CF ₃	Cl	H	CF ₃	OCH ₂ CF ₃	H
OCF ₃	Cl	H	OCF ₃	OCH ₂ CF ₃	H
OCF ₂ H	Cl	H	OCF ₂ H	OCH ₂ CF ₃	H
OSO ₂ CF ₃	Cl	H	OSO ₂ CF ₃	OCH ₂ CF ₃	H
Cl	Br	H	Cl	OCF ₂ H	H
Br	Br	H	Br	OCF ₂ H	H
CF ₃	Br	H	CF ₃	OCF ₂ H	H
OCF ₃	Br	H	OCF ₃	OCF ₂ H	H
OCF ₂ H	Br	H	OCF ₂ H	OCF ₂ H	H
OSO ₂ CF ₃	Br	H	OSO ₂ CF ₃	OCF ₂ H	H
Cl	CF ₃	H	Cl	CN	H
Br	CF ₃	H	Br	CN	H
CF ₃	CF ₃	H	CF ₃	CN	H
OCF ₃	CF ₃	H	OCF ₃	CN	H
OCF ₂ H	CF ₃	H	OCF ₂ H	CN	H
OSO ₂ CF ₃	CF ₃	H	OSO ₂ CF ₃	CN	H
Cl	F	H	Cl	OCH ₃	H
Br	F	H	Br	OCH ₃	H
CF ₃	F	H	CF ₃	OCH ₃	H
OCF ₃	F	H	OCF ₃	OCH ₃	H
OCF ₂ H	F	H	OCF ₂ H	OCH ₃	H
OSO ₂ CF ₃	F	H	OSO ₂ CF ₃	OCH ₃	H

TABLE 3

R ¹	R ²	R ⁷	R ¹	R ²	R ⁷
Cl	Cl	H	Cl	OCH ₂ CF ₃	H
Br	Cl	H	Br	OCH ₂ CF ₃	H
CF ₃	Cl	H	CF ₃	OCH ₂ CF ₃	H
OCF ₃	Cl	H	OCF ₃	OCH ₂ CF ₃	H
OCF ₂ H	Cl	H	OCF ₂ H	OCH ₂ CF ₃	H
OSO ₂ CF ₃	Cl	H	OSO ₂ CF ₃	OCH ₂ CF ₃	H
Cl	Br	H	Cl	OCF ₂ H	H
Br	Br	H	Br	OCF ₂ H	H
CF ₃	Br	H	CF ₃	OCF ₂ H	H
OCF ₃	Br	H	OCF ₃	OCF ₂ H	H
OCF ₂ H	Br	H	OCF ₂ H	OCF ₂ H	H
OSO ₂ CF ₃	Br	H	OSO ₂ CF ₃	OCF ₂ H	H
Cl	CF ₃	H	Cl	CN	H
Br	CF ₃	H	Br	CN	H
CF ₃	CF ₃	H	CF ₃	CN	H
OCF ₃	CF ₃	H	OCF ₃	CN	H
OCF ₂ H	CF ₃	H	OCF ₂ H	CN	H
OSO ₂ CF ₃	CF ₃	H	OSO ₂ CF ₃	CN	H
Cl	F	H	Cl	OCH ₃	H
Br	F	H	Br	OCH ₃	H
CF ₃	F	H	CF ₃	OCH ₃	H
OCF ₃	F	H	OCF ₃	OCH ₃	H
OCF ₂ H	F	H	OCF ₂ H	OCH ₃	H
OSO ₂ CF ₃	F	H	OSO ₂ CF ₃	OCH ₃	H

R ¹	R ²	R ⁷	R ¹	R ²	R ⁷
Cl	Cl	Me	Cl	OCH ₂ CF ₃	Me
Br	Cl	Me	Br	OCH ₂ CF ₃	Me
CF ₃	Cl	Me	CF ₃	OCH ₂ CF ₃	Me
OCF ₃	Cl	Me	OCF ₃	OCH ₂ CF ₃	Me
OCF ₂ H	Cl	Me	OCF ₂ H	OCH ₂ CF ₃	Me
OSO ₂ CF ₃	Cl	Me	OSO ₂ CF ₃	OCH ₂ CF ₃	Me
Cl	Br	Me	Cl	OCF ₂ H	Me
Br	Br	Me	Br	OCF ₂ H	Me
CF ₃	Br	Me	CF ₃	OCF ₂ H	Me
OCF ₃	Br	Me	OCF ₃	OCF ₂ H	Me
OCF ₂ H	Br	Me	OCF ₂ H	OCF ₂ H	Me
OSO ₂ CF ₃	Br	Me	OSO ₂ CF ₃	OCF ₂ H	Me
Cl	CF ₃	Me	Cl	CN	Me
Br	CF ₃	Me	Br	CN	Me
CF ₃	CF ₃	Me	CF ₃	CN	Me
OCF ₃	CF ₃	Me	OCF ₃	CN	Me
OCF ₂ H	CF ₃	Me	OCF ₂ H	CN	Me
OSO ₂ CF ₃	CF ₃	Me	OSO ₂ CF ₃	CN	Me
Cl	F	Me	Cl	OCH ₃	Me
Br	F	Me	Br	OCH ₃	Me
CF ₃	F	Me	CF ₃	OCH ₃	Me
OCF ₃	F	Me	OCF ₃	OCH ₃	Me
OCF ₂ H	F	Me	OCF ₂ H	OCH ₃	Me
OSO ₂ CF ₃	F	Me	OSO ₂ CF ₃	OCH ₃	Me

TABLE 4

R ¹	R ²	R ⁸	R ¹	R ²	R ⁸
Cl	Cl	H	Cl	OCH ₂ CF ₃	H
Br	Cl	H	Br	OCH ₂ CF ₃	H
CF ₃	Cl	H	CF ₃	OCH ₂ CF ₃	H
OCF ₃	Cl	H	OCF ₃	OCH ₂ CF ₃	H
OCF ₂ H	Cl	H	OCF ₂ H	OCH ₂ CF ₃	H
OSO ₂ CF ₃	Cl	H	OSO ₂ CF ₃	OCH ₂ CF ₃	H
Cl	Br	H	Cl	OCF ₂ H	H
Br	Br	H	Br	OCF ₂ H	H
CF ₃	Br	H	CF ₃	OCF ₂ H	H
OCF ₃	Br	H	OCF ₃	OCF ₂ H	H
OCF ₂ H	Br	H	OCF ₂ H	OCF ₂ H	H
OSO ₂ CF ₃	Br	H	OSO ₂ CF ₃	OCF ₂ H	H
Cl	CF ₃	H	Cl	CN	H
Br	CF ₃	H	Br	CN	H
CF ₃	CF ₃	H	CF ₃	CN	H
OCF ₃	CF ₃	H	OCF ₃	CN	H
OCF ₂ H	CF ₃	H	OCF ₂ H	CN	H
OSO ₂ CF ₃	CF ₃	H	OSO ₂ CF ₃	CN	H
Cl	F	H	Cl	OCH ₃	H
Br	F	H	Br	OCH ₃	H
CF ₃	F	H	CF ₃	OCH ₃	H
OCF ₃	F	H	OCF ₃	OCH ₃	H
OCF ₂ H	F	H	OCF ₂ H	OCH ₃	H
OSO ₂ CF ₃	F	H	OSO ₂ CF ₃	OCH ₃	H

TABLE 5

R ¹	R ²	R ⁷	R ¹	R ²	R ⁷
Cl	Cl	H	Cl	OCH ₂ CF ₃	H
Br	Cl	H	Br	OCH ₂ CF ₃	H
CF ₃	Cl	H	CF ₃	OCH ₂ CF ₃	H
OCF ₃	Cl	H	OCF ₃	OCH ₂ CF ₃	H
OCF ₂ H	Cl	H	OCF ₂ H	OCH ₂ CF ₃	H
OSO ₂ CF ₃	Cl	H	OSO ₂ CF ₃	OCH ₂ CF ₃	H
Cl	Br	H	Cl	OCF ₂ H	H
Br	Br	H	Br	OCF ₂ H	H
CF ₃	Br	H	CF ₃	OCF ₂ H	H
OCF ₃	Br	H	OCF ₃	OCF ₂ H	H
OCF ₂ H	Br	H	OCF ₂ H	OCF ₂ H	H
OSO ₂ CF ₃	Br	H	OSO ₂ CF ₃	OCF ₂ H	H
Cl	CF ₃	H	Cl	CN	H
Br	CF ₃	H	Br	CN	H
CF ₃	CF ₃	H	CF ₃	CN	H
OCF ₃	CF ₃	H	OCF ₃	CN	H
OCF ₂ H	CF ₃	H	OCF ₂ H	CN	H
OSO ₂ CF ₃	CF ₃	H	OSO ₂ CF ₃	CN	H
Cl	F	H	Cl	OCH ₃	H
Br	F	H	Br	OCH ₃	H
CF ₃	F	H	CF ₃	OCH ₃	H
OCF ₃	F	H	OCF ₃	OCH ₃	H
OCF ₂ H	F	H	OCF ₂ H	OCH ₃	H
OSO ₂ CF ₃	F	H	OSO ₂ CF ₃	OCH ₃	H

R ¹	R ²	R ⁷	R ¹	R ²	R ⁷
Cl	Cl	Me	Cl	OCH ₂ CF ₃	Me
Br	Cl	Me	Br	OCH ₂ CF ₃	Me
CF ₃	Cl	Me	CF ₃	OCH ₂ CF ₃	Me
OCF ₃	Cl	Me	OCF ₃	OCH ₂ CF ₃	Me
OCF ₂ H	Cl	Me	OCF ₂ H	OCH ₂ CF ₃	Me
OSO ₂ CF ₃	Cl	Me	OSO ₂ CF ₃	OCH ₂ CF ₃	Me
Cl	Br	Me	Cl	OCF ₂ H	Me
Br	Br	Me	Br	OCF ₂ H	Me
CF ₃	Br	Me	CF ₃	OCF ₂ H	Me
OCF ₃	Br	Me	OCF ₃	OCF ₂ H	Me
OCF ₂ H	Br	Me	OCF ₂ H	OCF ₂ H	Me
OSO ₂ CF ₃	Br	Me	OSO ₂ CF ₃	OCF ₂ H	Me
Cl	CF ₃	Me	Cl	CN	Me
Br	CF ₃	Me	Br	CN	Me
CF ₃	CF ₃	Me	CF ₃	CN	Me
OCF ₃	CF ₃	Me	OCF ₃	CN	Me
OCF ₂ H	CF ₃	Me	OCF ₂ H	CN	Me
OSO ₂ CF ₃	CF ₃	Me	OSO ₂ CF ₃	CN	Me
Cl	F	Me	Cl	OCH ₃	Me
Br	F	Me	Br	OCH ₃	Me
CF ₃	F	Me	CF ₃	OCH ₃	Me
OCF ₃	F	Me	OCF ₃	OCH ₃	Me
OCF ₂ H	F	Me	OCF ₂ H	OCH ₃	Me
OSO ₂ CF ₃	F	Me	OSO ₂ CF ₃	OCH ₃	Me

TABLE 6

R ¹	R ³	R ⁷	R ¹	R ³	R ⁷
Cl	Cl	H	Cl	OCH ₂ CF ₃	H
Br	Cl	H	Br	OCH ₂ CF ₃	H
CF ₃	Cl	H	CF ₃	OCH ₂ CF ₃	H
OCF ₃	Cl	H	OCF ₃	OCH ₂ CF ₃	H
OCF ₂ H	Cl	H	OCF ₂ H	OCH ₂ CF ₃	H
OSO ₂ CF ₃	Cl	H	OSO ₂ CF ₃	OCH ₂ CF ₃	H
Cl	Br	H	Cl	OCF ₂ H	H
Br	Br	H	Br	OCF ₂ H	H
CF ₃	Br	H	CF ₃	OCF ₂ H	H
OCF ₃	Br	H	OCF ₃	OCF ₂ H	H
OCF ₂ H	Br	H	OCF ₂ H	OCF ₂ H	H
OSO ₂ CF ₃	Br	H	OSO ₂ CF ₃	OCF ₂ H	H
Cl	CF ₃	H	Cl	CN	H
Br	CF ₃	H	Br	CN	H
CF ₃	CF ₃	H	CF ₃	CN	H
OCF ₃	CF ₃	H	OCF ₃	CN	H
OCF ₂ H	CF ₃	H	OCF ₂ H	CN	H
OSO ₂ CF ₃	CF ₃	H	OSO ₂ CF ₃	CN	H
Cl	F	H	Cl	OCH ₃	H
Br	F	H	Br	OCH ₃	H
CF ₃	F	H	CF ₃	OCH ₃	H
OCF ₃	F	H	OCF ₃	OCH ₃	H
OCF ₂ H	F	H	OCF ₂ H	OCH ₃	H
OSO ₂ CF ₃	F	H	OSO ₂ CF ₃	OCH ₃	H

R ¹	R ³	R ⁷	R ¹	R ³	R ⁷
Cl	Cl	Me	Cl	OCH ₂ CF ₃	Me
Br	Cl	Me	Br	OCH ₂ CF ₃	Me
CF ₃	Cl	Me	CF ₃	OCH ₂ CF ₃	Me
OCF ₃	Cl	Me	OCF ₃	OCH ₂ CF ₃	Me
OCF ₂ H	Cl	Me	OCF ₂ H	OCH ₂ CF ₃	Me
OSO ₂ CF ₃	Cl	Me	OSO ₂ CF ₃	OCH ₂ CF ₃	Me
Cl	Br	Me	Cl	OCF ₂ H	Me
Br	Br	Me	Br	OCF ₂ H	Me
CF ₃	Br	Me	CF ₃	OCF ₂ H	Me
OCF ₃	Br	Me	OCF ₃	OCF ₂ H	Me
OCF ₂ H	Br	Me	OCF ₂ H	OCF ₂ H	Me
OSO ₂ CF ₃	Br	Me	OSO ₂ CF ₃	OCF ₂ H	Me
Cl	CF ₃	Me	Cl	CN	Me
Br	CF ₃	Me	Br	CN	Me
CF ₃	CF ₃	Me	CF ₃	CN	Me
OCF ₃	CF ₃	Me	OCF ₃	CN	Me
OCF ₂ H	CF ₃	Me	OCF ₂ H	CN	Me
OSO ₂ CF ₃	CF ₃	Me	OSO ₂ CF ₃	CN	Me
Cl	F	Me	Cl	OCH ₃	Me
Br	F	Me	Br	OCH ₃	Me
CF ₃	F	Me	CF ₃	OCH ₃	Me
OCF ₃	F	Me	OCF ₃	OCH ₃	Me
OCF ₂ H	F	Me	OCF ₂ H	OCH ₃	Me
OSO ₂ CF ₃	F	Me	OSO ₂ CF ₃	OCH ₃	Me

TABLE 7

R ¹	R ³	R ⁷	R ¹	R ³	R ⁷
Cl	Cl	H	Cl	OCH ₂ CF ₃	H
Br	Cl	H	Br	OCH ₂ CF ₃	H
CF ₃	Cl	H	CF ₃	OCH ₂ CF ₃	H
OCF ₃	Cl	H	OCF ₃	OCH ₂ CF ₃	H
OCF ₂ H	Cl	H	OCF ₂ H	OCH ₂ CF ₃	H
OSO ₂ CF ₃	Cl	H	OSO ₂ CF ₃	OCH ₂ CF ₃	H
Cl	Br	H	Cl	OCF ₂ H	H
Br	Br	H	Br	OCF ₂ H	H
CF ₃	Br	H	CF ₃	OCF ₂ H	H
OCF ₃	Br	H	OCF ₃	OCF ₂ H	H
OCF ₂ H	Br	H	OCF ₂ H	OCF ₂ H	H
OSO ₂ CF ₃	Br	H	OSO ₂ CF ₃	OCF ₂ H	H
Cl	CF ₃	H	Cl	CN	H
Br	CF ₃	H	Br	CN	H
CF ₃	CF ₃	H	CF ₃	CN	H
OCF ₃	CF ₃	H	OCF ₃	CN	H
OCF ₂ H	CF ₃	H	OCF ₂ H	CN	H
OSO ₂ CF ₃	CF ₃	H	OSO ₂ CF ₃	CN	H
Cl	F	H	Cl	OCH ₃	H
Br	F	H	Br	OCH ₃	H
CF ₃	F	H	CF ₃	OCH ₃	H
OCF ₃	F	H	OCF ₃	OCH ₃	H
OCF ₂ H	F	H	OCF ₂ H	OCH ₃	H
OSO ₂ CF ₃	F	H	OSO ₂ CF ₃	OCH ₃	H

R ¹	R ³	R ⁷	R ¹	R ³	R ⁷
Cl	Cl	Me	Cl	OCH ₂ CF ₃	Me
Br	Cl	Me	Br	OCH ₂ CF ₃	Me
CF ₃	Cl	Me	CF ₃	OCH ₂ CF ₃	Me
OCF ₃	Cl	Me	OCF ₃	OCH ₂ CF ₃	Me
OCF ₂ H	Cl	Me	OCF ₂ H	OCH ₂ CF ₃	Me
OSO ₂ CF ₃	Cl	Me	OSO ₂ CF ₃	OCH ₂ CF ₃	Me
Cl	Br	Me	Cl	OCF ₂ H	Me
Br	Br	Me	Br	OCF ₂ H	Me
CF ₃	Br	Me	CF ₃	OCF ₂ H	Me
OCF ₃	Br	Me	OCF ₃	OCF ₂ H	Me
OCF ₂ H	Br	Me	OCF ₂ H	OCF ₂ H	Me
OSO ₂ CF ₃	Br	Me	OSO ₂ CF ₃	OCF ₂ H	Me
Cl	CF ₃	Me	Cl	CN	Me
Br	CF ₃	Me	Br	CN	Me
CF ₃	CF ₃	Me	CF ₃	CN	Me
OCF ₃	CF ₃	Me	OCF ₃	CN	Me
OCF ₂ H	CF ₃	Me	OCF ₂ H	CN	Me
OSO ₂ CF ₃	CF ₃	Me	OSO ₂ CF ₃	CN	Me
Cl	F	Me	Cl	OCH ₃	Me
Br	F	Me	Br	OCH ₃	Me
CF ₃	F	Me	CF ₃	OCH ₃	Me
OCF ₃	F	Me	OCF ₃	OCH ₃	Me
OCF ₂ H	F	Me	OCF ₂ H	OCH ₃	Me
OSO ₂ CF ₃	F	Me	OSO ₂ CF ₃	OCH ₃	Me

TABLE 8

R ¹	R ²	R ³	R ¹	R ²	R ³
Br	Cl	H	Br	OCH ₂ CF ₃	H
CF ₃	Cl	H	CF ₃	OCH ₂ CF ₃	H
OCF ₃	Cl	H	OCF ₃	OCH ₂ CF ₃	H
OCF ₂ H	Cl	H	OCF ₂ H	OCH ₂ CF ₃	H
OSO ₂ CF ₃	Cl	H	OSO ₂ CF ₃	OCH ₂ CF ₃	H
Br	Br	H	Br	OCF ₂ H	H
CF ₃	Br	H	CF ₃	OCF ₂ H	H
OCF ₃	Br	H	OCF ₃	OCF ₂ H	H
OCF ₂ H	Br	H	OCF ₂ H	OCF ₂ H	H
OSO ₂ CF ₃	Br	H	OSO ₂ CF ₃	OCF ₂ H	H
Br	CF ₃	H	Br	CN	H
CF ₃	CF ₃	H	CF ₃	CN	H
OCF ₃	CF ₃	H	OCF ₃	CN	H
OCF ₂ H	CF ₃	H	OCF ₂ H	CN	H
OSO ₂ CF ₃	CF ₃	H	OSO ₂ CF ₃	CN	H
Br	F	H	Br	OCH ₃	H
CF ₃	F	H	CF ₃	OCH ₃	H
OCF ₃	F	H	OCF ₃	OCH ₃	H
OCF ₂ H	F	H	OCF ₂ H	OCH ₃	H
OSO ₂ CF ₃	F	H	OSO ₂ CF ₃	OCH ₃	H

TABLE 9

R ¹	R ²	R ³	R ¹	R ²	R ³
Cl	Cl	H	Cl	OCH ₂ CF ₃	H
Br	Cl	H	Br	OCH ₂ CF ₃	H
CF ₃	Cl	H	CF ₃	OCH ₂ CF ₃	H
OCF ₃	Cl	H	OCF ₃	OCH ₂ CF ₃	H
OCF ₂ H	Cl	H	OCF ₂ H	OCH ₂ CF ₃	H
OSO ₂ CF ₃	Cl	H	OSO ₂ CF ₃	OCH ₂ CF ₃	H
Cl	Br	H	Cl	OCF ₂ H	H
Br	Br	H	Br	OCF ₂ H	H
CF ₃	Br	H	CF ₃	OCF ₂ H	H
OCF ₃	Br	H	OCF ₃	OCF ₂ H	H
OCF ₂ H	Br	H	OCF ₂ H	OCF ₂ H	H
OSO ₂ CF ₃	Br	H	OSO ₂ CF ₃	OCF ₂ H	H
Cl	CF ₃	H	Cl	CN	H
Br	CF ₃	H	Br	CN	H
CF ₃	CF ₃	H	CF ₃	CN	H
OCF ₃	CF ₃	H	OCF ₃	CN	H
OCF ₂ H	CF ₃	H	OCF ₂ H	CN	H
OSO ₂ CF ₃	CF ₃	H	OSO ₂ CF ₃	CN	H
Cl	F	H	Cl	OCH ₃	H
Br	F	H	Br	OCH ₃	H
CF ₃	F	H	CF ₃	OCH ₃	H
OCF ₃	F	H	OCF ₃	OCH ₃	H
OCF ₂ H	F	H	OCF ₂ H	OCH ₃	H
OSO ₂ CF ₃	F	H	OSO ₂ CF ₃	OCH ₃	H

TABLE 10

R ¹	R ²	R ³	R ¹	R ²	R ³
Br	Cl	H	Br	OCH ₂ CF ₃	H
CF ₃	Cl	H	CF ₃	OCH ₂ CF ₃	H
OCF ₃	Cl	H	OCF ₃	OCH ₂ CF ₃	H
OCF ₂ H	Cl	H	OCF ₂ H	OCH ₂ CF ₃	H
OSO ₂ CF ₃	Cl	H	OSO ₂ CF ₃	OCH ₂ CF ₃	H
Br	Br	H	Br	OCF ₂ H	H
CF ₃	Br	H	CF ₃	OCF ₂ H	H
OCF ₃	Br	H	OCF ₃	OCF ₂ H	H
OCF ₂ H	Br	H	OCF ₂ H	OCF ₂ H	H
OSO ₂ CF ₃	Br	H	OSO ₂ CF ₃	OCF ₂ H	H
Br	CF ₃	H	Br	CN	H
CF ₃	CF ₃	H	CF ₃	CN	H
OCF ₃	CF ₃	H	OCF ₃	CN	H
OCF ₂ H	CF ₃	H	OCF ₂ H	CN	H
OSO ₂ CF ₃	CF ₃	H	OSO ₂ CF ₃	CN	H
Br	F	H	Br	OCH ₃	H
CF ₃	F	H	CF ₃	OCH ₃	H
OCF ₃	F	H	OCF ₃	OCH ₃	H
OCF ₂ H	F	H	OCF ₂ H	OCH ₃	H
OSO ₂ CF ₃	F	H	OSO ₂ CF ₃	OCH ₃	H

TABLE 11

R ¹	R ²	R ³	R ¹	R ²	R ³
Cl	Cl	H	Cl	OCH ₂ CF ₃	H
Br	Cl	H	Br	OCH ₂ CF ₃	H
CF ₃	Cl	H	CF ₃	OCH ₂ CF ₃	H
OCF ₃	Cl	H	OCF ₃	OCH ₂ CF ₃	H
OCF ₂ H	Cl	H	OCF ₂ H	OCH ₂ CF ₃	H
OSO ₂ CF ₃	Cl	H	OSO ₂ CF ₃	OCH ₂ CF ₃	H
Cl	Br	H	Cl	OCF ₂ H	H
Br	Br	H	Br	OCF ₂ H	H
CF ₃	Br	H	CF ₃	OCF ₂ H	H
OCF ₃	Br	H	OCF ₃	OCF ₂ H	H
OCF ₂ H	Br	H	OCF ₂ H	OCF ₂ H	H
OSO ₂ CF ₃	Br	H	OSO ₂ CF ₃	OCF ₂ H	H
Cl	CF ₃	H	Cl	CN	H
Br	CF ₃	H	Br	CN	H
CF ₃	CF ₃	H	CF ₃	CN	H
OCF ₃	CF ₃	H	OCF ₃	CN	H
OCF ₂ H	CF ₃	H	OCF ₂ H	CN	H
OSO ₂ CF ₃	CF ₃	H	OSO ₂ CF ₃	CN	H
Cl	F	H	Cl	OCH ₃	H
Br	F	H	Br	OCH ₃	H
CF ₃	F	H	CF ₃	OCH ₃	H
OCF ₃	F	H	OCF ₃	OCH ₃	H
OCF ₂ H	F	H	OCF ₂ H	OCH ₃	H
OSO ₂ CF ₃	F	H	OSO ₂ CF ₃	OCH ₃	H

TABLE 12

R ¹	R ²	R ³	R ¹	R ²	R ³
Br	Cl	H	Br	OCH ₂ CF ₃	H
CF ₃	Cl	H	CF ₃	OCH ₂ CF ₃	H
OCF ₃	Cl	H	OCF ₃	OCH ₂ CF ₃	H
OCF ₂ H	Cl	H	OCF ₂ H	OCH ₂ CF ₃	H
OSO ₂ CF ₃	Cl	H	OSO ₂ CF ₃	OCH ₂ CF ₃	H
Br	Br	H	Br	OCF ₂ H	H
CF ₃	Br	H	CF ₃	OCF ₂ H	H
OCF ₃	Br	H	OCF ₃	OCF ₂ H	H
OCF ₂ H	Br	H	OCF ₂ H	OCF ₂ H	H
OSO ₂ CF ₃	Br	H	OSO ₂ CF ₃	OCF ₂ H	H
Br	CF ₃	H	Br	CN	H
CF ₃	CF ₃	H	CF ₃	CN	H
OCF ₃	CF ₃	H	OCF ₃	CN	H
OCF ₂ H	CF ₃	H	OCF ₂ H	CN	H
OSO ₂ CF ₃	CF ₃	H	OSO ₂ CF ₃	CN	H
Br	F	H	Br	OCH ₃	H
CF ₃	F	H	CF ₃	OCH ₃	H
OCF ₃	F	H	OCF ₃	OCH ₃	H
OCF ₂ H	F	H	OCF ₂ H	OCH ₃	H
OSO ₂ CF ₃	F	H	OSO ₂ CF ₃	OCH ₃	H

5 Formulation and Use

The compounds of this invention will generally be used in formulation with an agriculturally suitable carrier comprising a liquid or solid diluent or an organic solvent. Useful formulations of the compounds of Formula I can be prepared in conventional ways. They include dusts, granules, baits, pellets, solutions, suspensions, emulsions, wettable powders, emulsifiable concentrates, dry flowables and the like. Many of these can be applied directly. Sprayable formulations can be extended in suitable media and used at spray volumes of from about one to several hundred liters per hectare. High strength compositions are primarily used as intermediates for further formulation. The formulations, broadly, contain from less than about 1% to 99% by weight of active ingredient(s) and at least one of a) about 0.1% to 20% surfactant(s) and b) about 5% to 99% solid or liquid diluent(s). More specifically, they will contain effective amounts of these ingredients in the following approximate proportions:

		<u>Percent by Weight</u>		
		<u>Active</u>		
		<u>Ingredient</u>	<u>Diluent(s)</u>	<u>Surfactant(s)</u>
30	Wettable Powders	25-90	0-74	1-10
	Oil Suspensions, Emulsions, Solutions, (including Emulsifiable Concentrates)	5-50	40-95	0-15
35	Dusts	1-25	70-99	0-5
	Granules, Baits and Pellets	0.01-95	5-99	0-15
40	High Strength Compositions	90-99	0-10	0-2

5

Lower or higher levels of active ingredient can, of course, be present depending on the intended use and the physical properties of the compound. Higher ratios of surfactant to active ingredient are sometimes desirable, and are achieved by incorporation into the formulation or by tank mixing.

Typical solid diluents are described in Watkins, et al., "Handbook of Insecticide Dust Diluents and Carriers", 2nd Ed., Dorland Books, Caldwell, New Jersey. The more absorptive diluents are preferred for wettable powders and the denser ones for dusts. Typical liquid diluents and solvents are described in Marsden, "Solvents Guide," 2nd Ed., Interscience, New York, 1950. Solubility under 0.1% is preferred for suspension concentrates; solution concentrates are preferably stable against phase separation at 0°C. "McCutcheon's Detergents and Emulsifiers Annual", Allured Publ. Corp., Ridgewood, New Jersey, as well as Sisely and Wood, "Encyclopedia of Surface Active Agents", Chemical Publ. Co., Inc., New York, 1964, list surfactants and recommended uses. All formulations can contain minor amounts of additives to reduce foam, caking, corrosion, microbiological growth, etc. Preferably, ingredients should be approved by the U.S. Environmental Protection Agency for the use intended.

The methods of making such compositions are well known. Solutions are prepared by simply mixing the ingredients. Fine solid compositions are made by blending and, usually, grinding as in a hammer or fluid energy mill. Suspensions are prepared by wet milling (see, for example, U.S. 3,060,084). Granules and pellets can be made by spraying the active material upon

5 preformed granular carriers or by agglomeration
techniques. See J. E. Browning, "Agglomeration",
Chemical Engineering, December 4, 1967, pages 147 and
following, and "Perry's Chemical Engineer's Handbook",
4th Ed., McGraw-Hill, New York, 1963, pages 8 to 59 and
10 following.

Example A

Emulsifiable Concentrate

[1-(3-chlorophenyl)-2-phenylethylidene]-N-[4-
15 (trifluoromethyl)phenyl]hydrazinecarboxamide 20%
blend of oil soluble sulfonates and
polyoxyethylene ethers 10%
isophorone 70%

The ingredients are combined and stirred with gentle
20 warming to speed solution. A fine screen filter is
included in packaging operation to insure the absence of
any extraneous undissolved material in the product.

Example B

Wettable Powder

[1-(3-chlorophenyl)-2-phenylethylidene]-N-[4-
25 (trifluoromethyl)phenyl]hydrazinecarboxamide 30%
sodium alkylnaphthalenesulfonate 2%
sodium ligninsulfonate 2%
30 synthetic amorphous silica 3%
kaolinite 63%

The active ingredient is mixed with the inert
materials in a blender. After grinding in a hammermill,
the material is re-blended and sifted through a 50 mesh
35 screen.

5

Example CDust

Wettable powder of Example B 10%

pyrophyllite (powder) 90%

The wettable powder and the pyrophyllite diluent are thoroughly blended and then packaged. The product is suitable for use as a dust.

Example DGranule

15 [1-(3-chlorophenyl)-2-phenylethylidene]-N-[4-(trifluoromethyl)phenyl]hydrazinecarboxamide 10%

attapulgite granules (low volatile matter, 0.71/0.30 mm; U.S.S. No. 25-50 sieves) 90%

The active ingredient is dissolved in a volatile solvent such as acetone and sprayed upon dedusted and pre-warmed attapulgite granules in a double cone blender. The acetone is then driven off by heating. The granules are then allowed to cool and are packaged.

25

Example EGranule

Wettable powder of Example B 15%

gypsum 69%

potassium sulfate 16%

30 The ingredients are blended in a rotating mixer and water sprayed on to accomplish granulation. When most of the material has reached the desired range of 0.1 to 0.42 mm (U.S.S. No. 18 to 40 sieves), the granules are removed, dried, and screened. Oversize material is
35 crushed to produce additional material in the desired range. These granules contain 4.5% active ingredient.

5

Example FSolution

[1-(3-chlorophenyl)-2-phenylethylidene]-N-[4-(trifluoromethyl)phenyl]hydrazinecarboxamide 25%
N-methylpyrrolidone 75%

10 The ingredients are combined and stirred to produce a solution suitable for direct, low volume application.

Example GAqueous Suspension

15 [1-(3-chlorophenyl)-2-phenylethylidene]-N-[4-(trifluoromethyl)phenyl]hydrazinecarboxamide 40%
polyacrylic acid thickener 0.3%
dodecyclophenol polyethylene glycol ether 0.5%
disodium phosphate 1.0%
20 monosodium phosphate 0.5%
polyvinyl alcohol 1.0%
water 56.7%

The ingredients are blended and ground together in a sand mill to produce particles substantially all under 5.
25 microns in size.

Example HOil Suspension

[1-(3-chlorophenyl)-2-phenylethylidene]-N-[4-(trifluoromethyl)phenyl]hydrazinecarboxamide 35.0%
30 blend of polyalcohol carboxylic 6.0%
esters and oil soluble petroleum sulfonates
xylene range solvent 59.0%

35 The ingredients are combined and ground together in a sand mill to produce particles substantially all below

- 5 5 microns. The product can be used directly, extended with oils, or emulsified in water.

Example I

Bait Granules

- 10 [1-(3-chlorophenyl)-2-phenylethylidene]-N-[4-(trifluoromethyl)phenyl]hydrazinecarboxamide 3.0%
blend of polyethoxylated nonyl- 9.0%
phenols and sodium dodecylbenzene
sulfonates

- 15 ground up corn cobs 88.0%

The active ingredient and surfactant blend are dissolved in a suitable solvent such as acetone and sprayed onto the ground corn cobs. The granules are then dried and packaged.

- 20 Compounds of Formula I can also be mixed with one or more other insecticides, fungicides, nematocides, bactericides, acaricides, or other biologically active compounds to form a multi-component pesticide giving an even broader spectrum of effective agricultural
25 protection. Examples of other agricultural protectants with which compounds of this invention can be formulated are:

Insecticides:

- 30 3-hydroxy-N-methylcrotonamide (dimethylphosphate) ester (monocrotophos)
methylcarbamic acid, ester with 2,3-dihydro-2,2-dimethyl-7-benzofuranol (carbofuran)
O-[2,4,5-trichloro- α -(chloromethyl)benzyl]phosphoric
35 acid, O',O'-dimethyl ester (tetrachlorvinphos)
2-mercaptosuccinic acid, diethyl ester, S-ester with thionophosphoric acid, dimethyl ester (malathion)

- 5 phosphorothioic acid, O,O-dimethyl, O-p-nitrophenyl ester
(methyl parathion)
methylcarbamic acid, ester with α -naphthol (carbaryl)
methyl O-(methylcarbamoyl)thiolacetohydroxamate
(methomyl)
- 10 N'-(4-chloro-p-tolyl)-N,N-dimethylformamidine
(chlordimeform)
O,O-diethyl-O-(2-isopropyl-4-methyl-6-pyrimidylphos-
phorothioate (diazinon)
octachlorocamphene (toxaphene)
- 15 O-ethyl-O-p-nitrophenyl phenylphosphonothioate (EPN)
(S)- α -cyano-m-phenoxybenzyl (1R, 3R)-3-(2,2-dibromovinyl)-
2,2-dimethylcyclopropanecarboxylate (deltamethrin)
Methyl-N',N'-dimethyl-N-[(methylcarbamoyl)oxy]-1-thioox-
amimide (oxamyl)
- 20 cyano(3-phenoxyphenyl)-methyl-4-chloro-a-(1-methyl-
ethyl)benzeneacetate (fenvalerate)
(3-phenoxyphenyl)methyl (\pm)-~~cis,trans~~-3-(2,2-dichloro
ethenyl)-2,2-dimethylcyclopropanecarboxylate
(permethrin)
- 25 α -cyano-3-phenoxybenzyl 3-(2,2-dichlorovinyl)-2,2-
dimethylcyclopropane carboxylate (cypermethrin)
O-ethyl-S-(p-chlorophenyl)ethylphosphonodithioate
(profenofos)
phosphorothiolothionic acid, O-ethyl-O-[4-(methylthio)-
30 phenyl]-S-n-propyl ester (sulprofos)

Additional insecticides are listed hereafter by
their common names: triflumuron, diflubenzuron,
methoprene, buprofezin, thiodicarb, acephate,
35 azinphosmethyl, chlorpyrifos, dimethoate, fonophos,
isofenphos, methidathion, methamidophos, monocrotophos,
phosmet, phosphamidon, phosalone, pirimicarb, phorate,

- 5 terbufos, trichlorfon, methoxychlor, bifenthrin,
biphenate, cyfluthrin, fenpropathrin, fluvalinate,
flucythrinate, tralomethrin, metaldehyde and rotenone.

Fungicides:

- 10 methyl 2-benzimidazolecarbamate (carbendazim)
tetramethylthiuram disulfide (thiuram)
n-dodecylguanidine acetate (dodine)
manganese ethylenebisdithiocarbamate (maneb)
1,4-dichloro-2,5-dimethoxybenzene (chloroneb)
15 methyl 1-(butylcarbamoyl)-2-benzimidazolecarbamate
 (benomyl)
1-[2-(2,4-dichlorophenyl)-4-propyl-1,3-dioxolan-2-
 ylmethyl]-1H-1,2,4-triazole (propiconazole)
2-cyano-N-ethylcarbamoyl-2-methoxyiminoacetamide
20 (cymoxanil)
1-(4-chlorophenoxy)-3,3-dimethyl-1-(1H-1,2,4-triazol-1-
 yl)-2-butanone (triadimefon)
N-(trichloromethylthio)tetrahydrophthalimide (captan)
N-(trichloromethylthio)phthalimide (folpet)
25 1-[[[bis(4-fluorophenyl)][methyl]silyl]methyl]-1H-1,2,4-
 triazole

Nematocides:

- S-methyl 1-(dimethylcarbamoyl)-N-(methylcarbamoyloxy)-
30 thioformimidate
S-methyl 1-carbamoyl-N-(methylcarbamoyloxy)thio-
 formimidate
N-isopropylphosphoramidic acid O-ethyl O'-[4-(methyl-
 thio)-m-tolyl]diester (fenamiphos)

5 Bactericides:

tribasic copper sulfate
streptomycin sulfate

Acaricides:

- 10 senecioic acid, ester with 2-sec-butyl-4,6-dinitrophenol
(binapacryl)
6-methyl-1,3-cithiolo[4,5- β]quinoxalin-2-one
(oxythioquinox)
ethyl 4,4'-dichlorobenzilate (chlorobenzilate)
- 15 1,1-bis(p-chlorophenyl)-2,2,2-trichloroethanol (dicofol)
bis(pentachloro-2,4-cyclopentadien-1-yl) (dienochlor)
tricyclohexyltin hydroxide (cyhexatin)
trans-5-(4-chlorophenyl)-N-cyclohexyl-4-methyl-2-oxo-
thiazolidine-3-carboxamide (hexythiazox)
- 20 amitraz
propargite
fenbutatin-oxide

Biological

- 25 Bacillus thuringiensis
Avermectin B

Utility

- The compounds of this invention exhibit activity
- 30 against a wide spectrum of foliar and soil inhabiting
arthropods which are pests of growing and stored
agronomic crops, forestry, greenhouse crops, ornamentals,
nursery crops, stored food and fiber products, livestock,
household, and public and animal health. Those skilled
- 35 in the art will recognize that not all compounds are
equally effective against all agronomic and nonagronomic
pests but the compounds of this invention display

- 5 activity against economically important agronomic, forestry, greenhouse, ornamental food and fiber product, stored product, domestic structure, and nursery pests, such as:
- 10 larvae of the order Lepidoptera including fall and beet armyworm and other Spodoptera spp., tobacco budworm, corn earworm and other Heliothis spp., European corn borer, navel orangeworm, stalk/stem borers and other
- 15 pyralids, cabbage and soybean loopers and other loopers, codling moth, grape berry moth and other tortricids, black cutworm, spotted cutworm, other cutworms and other noctuids, diamondback moth, green cloverworm, velvetbean caterpillar, green cloverworm, pink bollworm,
- 20 gypsy moth, and spruce budworm;
- foliar feeding larvae and adults of the order Coleoptera including Colorado potato beetle,
- 25 Mexican bean beetle, flea beetle, Japanese beetles, and other leaf beetles, boll weevil, rice water weevil, granary weevil, rice weevil and other weevil pests, and soil inhabiting insects such as Western corn rootworm and other
- 30 Diabrotica spp., Japanese beetle, European chafer and other coleopteran grubs, and wireworms;
- adults and larvae of the orders Hemiptera and
- 35 Homoptera including tarnished plant bug and other plant bugs (miridae), aster leafhopper

5 and other leafhoppers (cicadellidae), rice
planthopper, brown planthopper, and other
planthoppers (fulgoroidea), psyllids, whiteflies
(aleurodidae), aphids (aphidae), scales
(coccidae and diaspididae), lace bugs
10 (tingidae), stink bugs (pentatomidae), cinch
bugs and other seed bugs (lygaeidae), cicadas
(cicadidae), spittlebugs (cercopids), squash
bugs (coreidae), red bugs and cotton stainers
(pyrrhocoridae);

15 adults and larvae of the order acari (mites)
including European red mite, two spotted spider
mite, rust mites, McDaniel mite, and foliar
feeding mites;

20 adults and immatures of the order Orthoptera
including grasshoppers;

adults and immatures of the order Diptera
25 including leafminers, midges, fruit flies
(tephritidae), and soil maggots;

adults and immatures of the order Thysanoptera
including onion thrips and other foliar feeding
30 thrips.

The compounds are also active against economically
important livestock, household, public and animal health
pests such as:

35 insect pests of the order Hymenoptera including
carpenter ants, bees, hornets, and wasps;

5

insect pests of the order Diptera including house flies, stable flies, face flies, horn flies, blow flies, and other muscoid fly pests, horse flies, deer flies and other Brachycera, mosquitoes, black flies, biting midges, sand flies, sciarids, and other Nematocera;

10

insect pests of the order Orthoptera including cockroaches and crickets;

15

insect pests of the order Isoptera including the Eastern subterranean termite and other termites; insect pests of the order Mallophaga and Anoplura including the head louse, body louse, chicken head louse and other sucking and chewing parasitic lice that attack man and animals;

20

insect pests of the order Siphonoptera including the cat flea, dog flea and other fleas.

25

The specific species for which control is exemplified are: fall armyworm, Spodoptera frugiperda; tobacco budworm, Heliothis virescens; boll weevil, Anthonomus grandis; aster leafhopper, Macrosteles fascifrons; black bean aphid, (Aphis fabae); southern corn rootworm, Diabrotica undecimpunctata. The pest control protection afforded by the compounds of the present invention is not limited, however, to these species. The compounds of this invention may also be utilized as rodenticides.

30

35

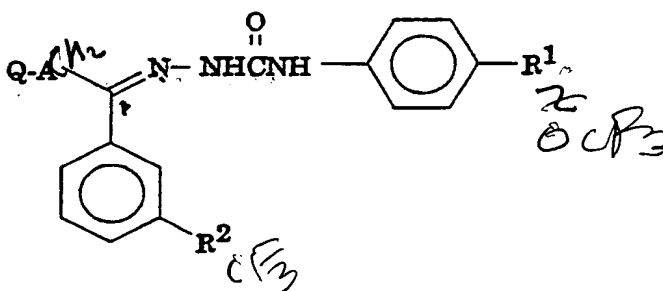
5 Application

Arthropod pests are controlled and protection of agronomic crops, animal and human health is achieved by applying one or more of the Formula I compounds, in an effective amount, to the environment of the pests including the agronomic and/or nonagronomic locus of infestation, to the area to be protected, or directly on the pests to be controlled. Because of the diversity of habitat and behavior of these arthropod pest species, many different methods of application are employed. A preferred method of application is by spraying with equipment that distributes the compound in the environment of the pests, on the foliage, animal, person, or premise, in the soil or animal, to the plant part that is infested or needs to be protected. Alternatively, granular formulations of these toxicant compounds can be applied to or incorporated into the soil. Other methods of application can also be employed including direct and residual sprays, aerial sprays, baits, eartags, boluses, foggers, aerosols, and many others. The compounds can be incorporated into baits that are consumed by the arthropods or in devices such as traps and the like which entice them to ingest or otherwise contact the compounds.

The compounds of this invention can be applied in their pure state, but most often application will be of a formulation comprising one or more compounds with suitable carriers, diluents, and surfactants and possibly in combination with a food depending on the contemplated end use. A preferred method of application involves spraying a water dispersion or refined oil solution of the compounds. Combinations with spray oils, spray oil concentrations, and synergists such as piperonyl butoxide often enhance the efficacy of the compounds of Formula I.

- 5 The rate of application required for effective control will depend on such factors as the species of arthropod to be controlled, the pest's life cycle, life stage, its size, location, time of year, host crop or animal, feeding behavior, mating behavior, ambient
10 moisture, temperature, etc. In general, application rates of 0.01 to 2 kg of active ingredient per hectare are sufficient to provide large-scale effective control of pests in agronomic ecosystems under normal
15 circumstances, but as little as 0.001 kg/hectare or as much as 8 kg hectare may be required. For nonagronomic applications, effective use rates will range from about 1.0 to 50 mg/square meter but as little as about 0.1
mg/square meter or as much as 150 mg/square meter may be required.
- 20 ~~The following tests demonstrate the control efficacy~~ of compounds of Formula I on specific pests; see Index Table A for compound descriptions. Compounds not included in the test result summaries were either not screened or produced less than the recited threshold
25 mortalities.

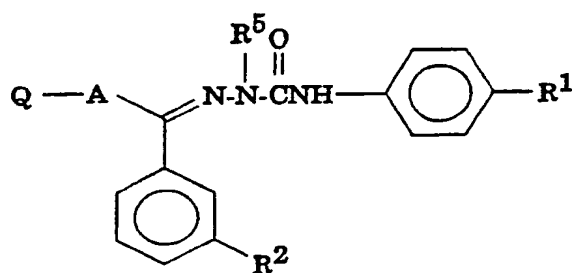
INDEX TABLE A



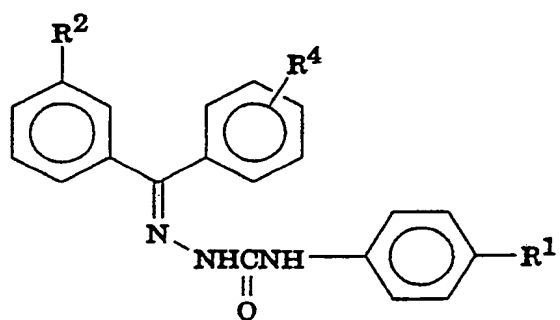
Compound	R ¹	R ²	A	Q	mp (°C)
1	CF ₃	Cl	CH ₂	Ph	225-229
2	OCF ₃	Cl	CH ₂	Ph	201-208
3	CF ₃	CF ₃	CH ₂	Ph	201-206
4	OCF ₃	CF₃	CH ₂	Ph	190-193
5	OCF ₃	CF ₃	CH ₂	4-F-Ph	164-171
6	CF ₃	CF ₃	CH ₂	n-Pr	160-162
7	OCF ₃	CF ₃	CH ₂	n-Pr	156-157
8	Cl	CF ₃	CH ₂	n-Pr	white solid
9	Br	CF ₃	CH ₂	n-Pr	white solid
10	CF ₃	Cl	CH ₂	Me	210-218
11	OCF ₃	Cl	CH ₂	Me	200-209
12	Cl	Cl	CH ₂	Me	220-237
13	Br	Cl	CH ₂	Me	white solid
14	CF ₃	CF ₃	CH ₂	Me	185-195
15	OCF ₃	CF ₃	CH ₂	Me	178-185
16	CF ₃	F	CH ₂	4-F-Ph	200-212
17	OCF ₃	F	CH ₂	4-F-Ph	180-189
18	CF ₃	CF ₃	CH ₂	4-F-Ph	185-193
19	CF ₃	Cl	CH ₂	4-F-Ph	204-208
20	OCF ₃	Cl	CH ₂	4-F-Ph	168-177
21	CF ₃	CF ₃	CH ₂	4-CF ₃ -Ph	145-169
22	OCF ₃	CF ₃	CH ₂	4-CF ₃ -Ph	160-170

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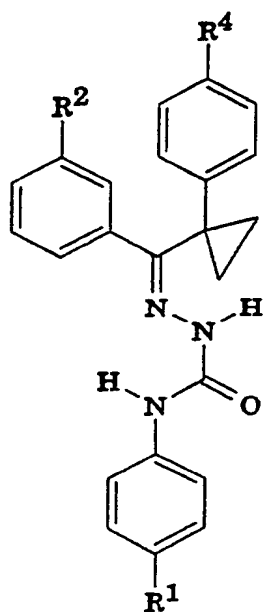
<u>Compound</u>	R^1	R^2	A	Q	<u>mp ($^{\circ}C$)</u>
23	CF ₃	CF ₃	CH ₂	i-Pr	185-190
24	OCF ₃	CF ₃	CH ₂	i-Pr	144-150
25	CF ₃	Cl	CH ₂	i-Pr	172-184
26	OCF ₃	Cl	CH ₂	i-Pr	158-163
27	CF ₃	CF ₃	CH (Me)	Me	145-151
28	OCF ₃	CF ₃	CH (Me)	Me	105-120
29	CF ₃	CF ₃	C (Me) ₂	Me	105-118
30	OCF ₃	CF ₃	C (Me) ₂	Me	105-115



<u>Compound</u>	R^1	R^2	R^5	A	Q	<u>Phys. Prop.</u>
31	CF ₃	CF ₃	CO ₂ Me	CH ₂	i-Pr	solid



<u>Compound</u>	R^1	R^2	R^4	<u>mp ($^{\circ}C$)</u>
32	CF_3	CF_3	3- CF_3	170-177
33	OCF_3	CF_3	3- CF_3	142-148
34	OCF_3	CF_3	4-F	160-170



<u>Compound</u>	<u>R¹</u>	<u>R²</u>	<u>R⁴</u>	<u>mp (°C)</u>
35	OCF ₃	H	H	148-150
36	OCF ₃	Cl	F	157-159
37	CF ₃	Cl	F	192-194
38	OCF ₃	Cl	H	186-188
39	CF ₃	Cl	H	210-212
40	OCF ₃	CF ₃	F	183-185
41	CF ₃	CF ₃	F	121-124

5 Insecticide Test ProtocolsCompound Application

Experimental compounds are formulated in a 75:25 acetone:water solution, unless otherwise indicated. All compounds are initially tested at 1000 ppm. The formulated compound is applied with a single, flat fan 8001E nozzle positioned 7.5 inches (19 cm) above the test units which are situated on a conveyor belt. Spray pressure is maintained at 30 psi (207 kPa), and the conveyor speed is adjusted so that 6 ml of test solution is sprayed per 0.1 square meter of conveyor at a rate of 0.5 pounds (0.2 kg) of active ingredient per acre (0.55 kg/ha). Three untreated (blanks) and three solvent-treated test units are run for each insect species tested.

20 EXAMPLE JFall Armyworm (FAW) Spodoptera frugiperda

Acute Toxicity: Two lima bean leaf discs, each with a surface area of 8.1 cm² were sprayed top side up along with 7-12 3rd instar, unstarved fall armyworm larvae. The treated lima bean leaves were placed top side up in a 15 mm x 100 mm petri dish that had been lined with filter paper moistened with 1.5 ml of water. After the leaf discs had dried, 5 sprayed larvae were introduced into the petri dish. Larval mortality was assessed at 48 hours post-treatment. Of the compounds tested, the following produced 80% mortality or greater: Compounds 1, 2, 3, 5, 6, 16, 17, 18, 20, 21, 22, 23, 24, 25, 26, 28, 31, 32, 33, 36, 37, 40 and 41*.

Antifeedant Test: At the 48 hour acute toxicity assessment, the amount of each leaf disc eaten was determined and expressed as percent reduction in feeding relative to controls. Of the compounds tested, the

- 5 following induced feeding reduction of 75% or greater:
Compound 1.

EXAMPLE K

Tobacco Budworm (TBW)

Heliothis virescens (helioverpa)

- 10 Five 3rd instar larvae were placed in an 8 oz (230
ml) cup containing artificial diet and sprayed with the
test solution. Larval mortality was assessed at 48 hours
post-treatment. Of the compounds tested, the following
produced 80% mortality or greater: Compounds 2, 3, 4, 5,
15 6, 7, 18, 20, 21, 22, 23, 24, 26, 27, 28, 31, 32, 33, 36,
37, 38, 40 and 41*.

EXAMPLE L

Southern Corn Rootworm (SCRW)

Diabrotica undecimpunctata howardi

- 20 An 8 oz (230 ml) dish containing a germinated corn
kernel was sprayed with the test solution. After the
spray had dried, five unsprayed, 3rd instar corn rootworm
larvae were placed in the dish along with a moistened
cotton wick. Larval mortality was assessed at 48 hours
25 post-treatment. Of the compounds tested, the following
produced 80% mortality or greater: Compounds 1, 2, 3, 4,
5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 17, 18, 19, 20,
23, 24, 25, 26, 27, 28, 31, 32, 35, 36, 37, 38, 39, 40
and 41*.

- 30 EXAMPLE M

Boll Weevil (BW) Anthonomus grandis grandis

- A filter paper-lined 9 oz (260 ml) plastic tumbler
containing 5 adult boll weevils was sprayed with the test
solution. The treated cups were capped with a paper lid
35 with an opening cut into it, and placed in a ventilated
room to dry for several hours. Mortality was assessed at
48 hours post-treatment. Of the compounds tested, the

5 following produced 80% mortality or greater: Compounds
3, 4, 5, 6, 7, 8, 9, 10, 12, 14, 15, 16, 17, 18, 19, 20,
22, 23, 24, 25, 26, 27, 28, 31, 33, 35, 36, 37, 38, 39,
40 and 41*.

EXAMPLE N

10 Aster Leafhopper (ALH) Macrosteles quadrilineatus
Six day old oat seedlings planted in a 12 oz (350
ml) cup with a layer of white sand covering the soil were
sprayed with the test solution. The treated test unit
was allowed to dry and then capped. Leafhoppers were
15 aspirated into the test unit through an opening in the
lid. At least 15 adult leafhoppers were introduced into
the test unit and the opening was sealed with a piece of
cotton gauze. Mortality was assessed at 48 hours post-
treatment. Of the compounds tested, the following
20 produced 80% mortality or greater: Compounds 1, 5, 23,
24, 25, 26, 28, 31, 36, 37 and 40.

*Compound tested at 250 ppm.

25

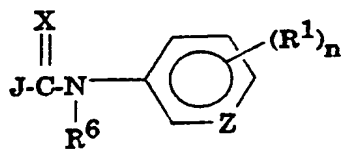
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CLAIMS

1. A compound of the formula

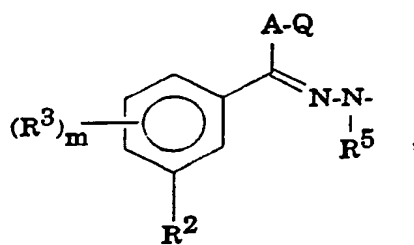


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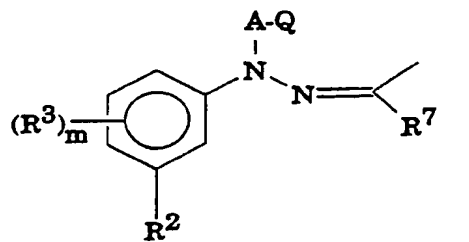
10

wherein

J is selected from the group

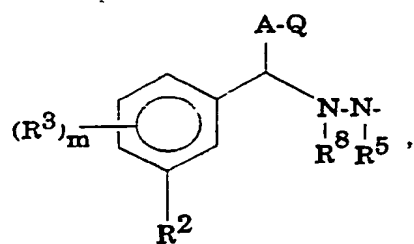


J-1

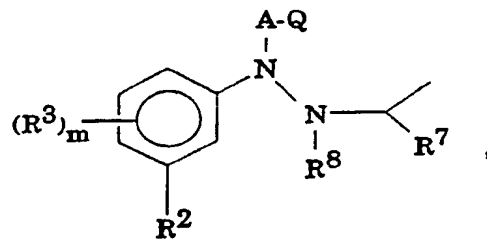


J-2

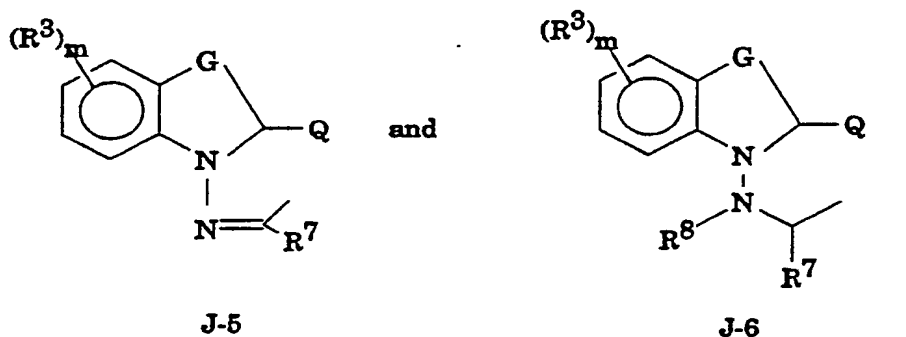
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J-3



J-4



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wherein

- A is a single bond or selected from the group
C₁-C₃ alkylene and C₃-C₆ cycloalkylene each of
which is optionally substituted with 1 or 2 R⁹;
- G is C₁-C₂ alkylene optionally substituted with 1
or 2 CH₃;
- Q is selected from the group H, R⁹, phenyl
optionally substituted with (R⁴)_p, thienyl
optionally substituted with W, pyridinyl
optionally substituted with W, C₁-C₆ alkyl
optionally substituted with R⁹ and C₃-C₆
cycloalkyl optionally substituted with R⁹;
provided that when J is J-1 and A is methylene,
then Q is other than H;
- X is selected from the group O and S;
- Z is selected from the group N and CH;
- R¹, R², R³ and R⁴ are independently selected from
the group halogen, CN, SCN, R¹⁰, OR¹⁰, S(O)_qR¹⁰,
OSO₂R¹⁰, C(O)R¹⁰, CO₂R¹⁰, C(O)N(R¹⁰)R¹¹,
SO₂N(R¹⁰)R¹¹ and N(R¹⁰)R¹¹; and when m, n or p is
2, (R¹)₂, (R³)₂, (R⁴)₂ or R² and R³ when
attached to adjacent atoms can be taken together
as OCH₂O, OCF₂O, OCH₂CH₂O, OCH₂C(CH₃)₂O or
OCF₂CF₂O to form a cyclic bridge; provided that
when R² is Cl then R³ is other than Cl;

30

- 5 R^5 and R^6 are independently selected from the group
H, C_1 - C_6 alkyl, C_2 - C_6 alkoxyalkyl, CHO, C_2 - C_6
alkylcarbonyl, C_2 - C_6 alkoxycarbonyl, C_2 - C_6
haloalkylcarbonyl, C_1 - C_6 alkylthio, C_1 - C_6
haloalkylthio, $R^{12}OC(O)N(R^{13})S-$, $R^{15}(R^{14})NS-$ and
10 benzyl optionally substituted with W;
 R^7 is selected from the group H, C_1 - C_6 alkyl, C_1 - C_6
haloalkyl and phenyl optionally substituted with
W;
 R^8 is selected from the group H, C_1 - C_3 alkyl,
15 CO_2R^{10} and $C(O)N(R^{10})R^{11}$;
 R^9 is selected from the group halogen, NO_2 , CN,
 C_1 - C_3 alkyl, C_1 - C_3 haloalkyl, OH, OR^{10} ,
 $S(O)_qR^{10}$, $N(H)R^{11}$, $N(R^{10})R^{11}$ and CO_2R^{10} ;
 R^{10} is selected from the group C_1 - C_4 alkyl, C_1 - C_4
20 haloalkyl, C_2 - C_4 alkenyl, C_2 - C_4 haloalkenyl,
 C_3 - C_4 alkynyl, C_3 - C_4 haloalkynyl, C_2 - C_6
alkoxyalkyl, C_2 - C_6 alkylthioalkyl, C_2 - C_6
cyanoalkyl, C_3 - C_6 alkoxycarbonyl alkyl, C_3 - C_6
cycloalkyl, C_3 - C_6 halocycloalkyl, C_4 - C_7
25 alkylcycloalkyl, C_4 - C_7 haloalkylcycloalkyl,
optionally substituted phenyl and optionally
substituted benzyl wherein the phenyl and benzyl
substituent(s) are 1 to 3 substituents
independently selected from W;
30 R^{11} is selected from the group H and C_1 - C_4 alkyl;
 R^{12} and R^{13} are independently selected from C_1 - C_6
alkyl;
 R^{14} and R^{15} are independently selected from C_1 - C_4
alkyl; or
35 R^{14} and R^{15} when attached to the same atom can be
taken together as $(CH_2)_5$ or $CH_2CH_2OCH_2CH_2$;

- 5 W is selected from the group halogen, CN, NO₂,
C₁-C₂ alkyl, C₁-C₂ haloalkyl, C₁-C₂ alkoxy,
C₁-C₂ haloalkoxy, C₁-C₃ alkylthio, C₁-C₂
haloalkylthio, C₁-C₂ alkylsulfonyl, and C₁-C₂
haloalkylsulfonyl;
- 10 m is 0 to 2;
 n is 1 to 2;
 p is 0 to 2; and
 q is 0 to 2.
- 15 2. A compound according to Claim 1 wherein:
- A is selected from the group C₁-C₃ alkylene
 and C₃-C₆ cycloalkylene each of which is
 optionally substituted with 1 or 2 R⁹;
- G is C₁-C₂ alkylene substituted with 1 or 2
20 CH₃;
- Q is selected from the group CO₂R¹⁰, phenyl
 optionally substituted with (R⁴)_p, C₁-C₆
 alkyl optionally substituted with R⁹ and
 C₃-C₆ cycloalkyl optionally substituted
25 with R⁹;
- X is O;
- R¹, R², R³ and R⁴ are independently selected
 from the group halogen, CN, R¹⁰, OR¹⁰,
 S(O)_qR¹⁰ and OSO₂R¹⁰;
- 30 R⁵ and R⁶ are independently selected from the
 group H, C₁-C₂ alkyl, C₂-C₃ alkylcarbonyl
 and C₂-C₃ alkoxycarbonyl;
- R⁷ is selected from the group H and CH₃;
- R⁸ is H;
- 35 R⁹ is selected from the group halogen, CN,
 C₁-C₃ alkyl, C₁-C₃ haloalkyl, OH, S(O)_qR¹⁰
 and CO₂R¹⁰;

5 R¹⁰ is selected from the group C₁-C₃ alkyl and
 C₁-C₃ haloalkyl;
 R¹¹ is selected from the group H or CH₃;
 W is selected from the group halogen, CN,
10 NO₂, C₁-C₂ alkyl, C₁-C₂ haloalkyl, C₁-C₂
 alkoxy, C₁-C₂ haloalkoxy, C₁-C₂ alkylthio,
 C₁-C₂ haloalkylthio, C₁-C₂ alkylsulfonyl,
 and C₁-C₂ haloalkylsulfonyl;
 m is 0 to 1;
 n is 1 with R¹ in the para-position;
15 p is 0 or 1; and
 q is 0 or 2.

- 20 3. A compound according to Claim 2 wherein J is
 J-1.
4. A compound according to Claim 2 wherein J is
 J-2.
- 25 5. A compound according to Claim 2 wherein J is
 J-3.
6. A compound according to Claim 2 wherein J is
 J-4.
- 30 7. A compound according to Claim 2 wherein J is
 J-5.
8. A compound according to Claim 2 wherein J is
 J-6.
- 35

5 9. A compound according to Claim 2 wherein A is
C₁-C₂ alkylene optionally substituted with 1 or 2 methyl
groups.

10 10. A compound according to Claim 3:
2-[2-phenyl-1-[3-trifluoromethyl)phenyl]-
ethylidene]-N-[4-(trifluoromethoxy)-
phenyl]hydrazine carboxamide.

15 11. An arthropodicidal composition comprising a
compound according to any one of Claims 1 to 10 and a
carrier therefor.

20 12. A method for controlling arthropods comprising
contacting them or their environment with an
arthropodically effective amount of a compound
according to any one of Claims 1 to 10.

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INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 91/07091

I. CLASSIFICATION OF SUBJECT MATTER (If several classification symbols apply, indicate all) ⁶		
According to International Patent Classification (IPC) or to both National Classification and IPC		
Int. Cl. 5	C07C281/14; C07D209/08;	C07C281/06; A01N47/34; C07C251/76; C07D209/42; C07C243/22 C07D215/58
II. FIELDS SEARCHED		
Minimum Documentation Searched ⁷		
Classification System	Classification Symbols	
Int. Cl. 5	C07C ; C07D	
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched ⁸		
III. DOCUMENTS CONSIDERED TO BE RELEVANT⁹		
Category ¹⁰	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³
A	GB,A,1 355 304 (CYANAMID) 5 June 1974 see claims; examples ---	1-10
A	GB,A,1 194 990 (BAYER) 17 June 1970 see claims; examples ---	1-12
A	US,A,3 182 082 (SYDOR) 4 May 1965 see whole document ---	1-10
A	GB,A,1 374 725 (PHILIPS) 20 November 1974 cited in the application see claims; examples ---	1-12
A	US,A,3 753 680 (TILLES) 21 August 1973 cited in the application see claims; examples ---	1-10
-/-		
<p>¹⁰ Special categories of cited documents : ¹⁰</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"&" document member of the same patent family</p>		
IV. CERTIFICATION		
Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report	
26 FEBRUARY 1992	I.M.HELPS 12. 03. 92	
International Searching Authority	Signature of Authorized Officer	
EUROPEAN PATENT OFFICE	HELPS I.M.	

III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)

Category *	Citation of Document, with indication, where appropriate, of the relevant passages	Relevant to Claim No.
A	EP,A,0 254 461 (SCHERING) 27 January 1988 cited in the application see whole document ---	1-10
A	EP,A,0 377 304 (DU PONT) 11 July 1990 cited in the application see claims; examples ---	1-12

**ANNEX TO THE INTERNATIONAL SEARCH REPORT
ON INTERNATIONAL PATENT APPLICATION NO. US 9107091
SA 53786**

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SA 53786**

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Page 2

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		CA-A- 2005740	27-06-90
		EP-A- 0452406	23-10-91
		WO-A- 9007495	12-07-90
		WO-A- 9107382	30-05-91